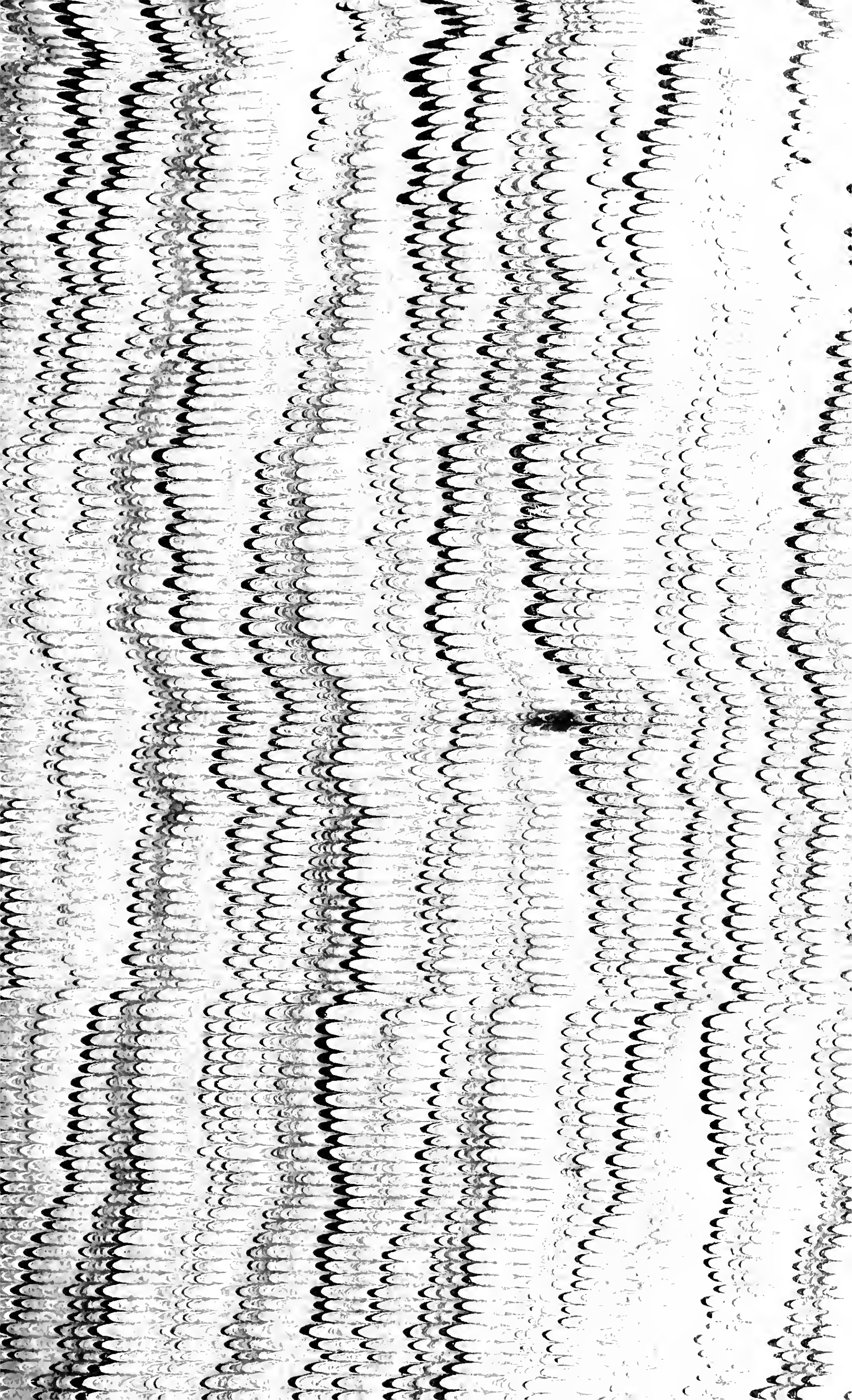

SMITHSONIAN

MISCELLANEOUS COLLECTIONS.

VOL. XXVII.

"EVERY MAN IS A VALUABLE MEMBER OF SOCIETY WHO BY HIS OBSERVATIONS, RESEARCHES, AND EXPERIMENTS PROCURES KNOWLEDGE FOR MEN."—SMITHSON.

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S. F. BAIRD,
Secretary S. I.

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SMITHSONIAN MISCELLANEOUS COLLECTIONS.

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THE CONSTANTS OF NATURE.

PART IV.

ATOMIC WEIGHT DETERMINATIONS:

A DIGEST OF THE INVESTIGATIONS PUBLISHED SINCE 1814.

BY

GEORGE F. BECKER.

WASHINGTON:
SMITHSONIAN INSTITUTION.
AUGUST, 1880.

ADVERTISEMENT.

The following forms the *fourth* part of a general work on the "CONSTANTS OF NATURE," of which the first three are as follows:

Part I and Supplement.—Specific Gravities, Boiling Points and Melting Points, by F. W. Clarke.

Part II.—A Table of Specific Heats for Solids and Liquids, by F. W. Clarke.

Part III.—Tables of Expansion by Heat for Solids and Liquids, by F. W. Clarke.

The manuscript of the present work has been presented to the Smithsonian Institution by Mr. G. F. Becker and is published at the expense of its fund.

S. F. BAIRD,
Secretary Smithsonian Institution.

WASHINGTON, AUGUST, 1880.

PREFACE.

Of the fundamental importance of the most accurate attainable knowledge concerning the true atomic weights of the elements there can be no two opinions. If the enormous mass of known facts relating to the properties of matter is ever to be brought under wide generalizations, it is with the simple substances that a beginning must be made, and with the simplest property of these substances, the relative weights of their ultimate particles. Berzelius held this view and the labors of Mendelejeff, Meyer and others leave no question as to the fact of a relation between the atomic weights and the properties of simple and compound matter. Accurate information on the subject, however, is not easily attainable; different writers on chemistry follow different authorities, and some even take a mean between the results arrived at by experimenters of different degrees of skill and accuracy, or assume some convenient number without experimental foundation. Nowhere, to my knowledge, is there even an approximately complete list of the determinations that have been made.

Forced back, myself, upon the original memoirs for information, I believed that I should do other chemists a service in presenting to them a short but systematic digest of each investigation on the subject, including the following points, so far as they could be ascertained: The nature of the material experimented upon, and the method of its preparation; the experimental method adopted to effect the determination, and the number of experiments; the mean result reached by the experiments, and the extreme difference between the results; such a record of the constants employed in the calculation as will enable any one to recalculate the results for different constants; and the place in literature where the original paper is to be found.

The following pages are the result. From the information

he will find in them, the experienced chemist will, in most cases, I think, be able to decide which determination offers the best guarantees for accuracy, or at least between which determinations his choice must lie, forming his judgment to a great extent independently of the comparative reputation of the observers—not always a safe guide where one is, in a general way, the unquestionable superior of the other—and no guide at all when the names carry on the whole an equal weight. As a record of the direction investigations have taken and of analytical methods of the most exact character also, I hope that this digest may not be without value.

As this compilation would serve rather to mislead than to assist investigators, unless it be accurate and practically exhaustive, it seems proper to explain the manner in which it has been prepared. Believing it best to work independently of any previous compilations, I selected as my base the three great German journals—*Poggendorff's Annalen*, *Liebig's Annalen*, and *Erdmann's Journal für Praktische Chemie*. My choice was determined not only by the position these journals take in chemico-physical science, but by the fact that their indices are admirable, and their tone cosmopolitan; all of them, until lately, having furnished their readers with the scientific news of the time, and with abstracts from and translations of the important papers published elsewhere and in whatever language, as well as with original investigations. The indices of these journals I read through from beginning to end, making an extract of every entry which bore on the subject of atomic weights, or which I suspected might do so. In studying the articles thus reached, every reference to other atomic weight determinations was preserved, and the originals, so far as possible, sought out; a task in which the Royal Society's *Catalogue of Scientific Papers* was of the greatest assistance. Having exhausted the supply of information in these journals, I turned to *Berzelius' Jahresbericht*, and to its continuation edited by *Kopp*, *Liebig et al.*, and made a study of their contents by the same method. Later, I made a similar systematic study of the *Annales de Chimie et de Physique*, the *Bericht der Deutschen Chemischen Gesellschaft*, the *Chemical*

News, *Fresenius' Zeitschrift für Analytische Chemie*, the *Journal of the Chemical Society*, the *Proceedings of the Royal Society*, and the *Philosophical Transactions*, and of *Silliman's American Journal of Science*. I have also made some use of the *Philosophical Magazine*, and a great deal of use of the *Paris Comptes Rendus*. These publications are not so indexed as to make their contents readily available; but what appears in the *Comptes Rendus* is pretty sure to be noticed elsewhere, and I scarcely think that any determinations there published have escaped me. I have also made use of the *Bibliothèque Universelle, Archives des Sciences* of Geneva, (an incomplete set, unfortunately,) the *Zeitschrift für Berg-Hütten-und Salinen-Wesen im Preussischen Staate*, *Thomson's Annals of Philosophy*, *Gilbert's Annalen der Physik und der Physikalischen Chemie*, the *British Association Reports*, the *Transactions of the Royal Society of Edinburgh*, the *Transactions of the Academies of Brussels* and of *St. Petersburg*, and have consulted numerous works on chemistry, particularly *Berzelius' Lehrbuch der Chemie* and *Gmelin-Kraut's Handbuch der Chemie*.

I have not thought it necessary, or even desirable, to extend my search for atomic weight determinations further back than Wollaston's famous "Table of Equivalents," published in the *Philosophical Transactions* for 1814. It is true that numerous determinations had been made before that time, but, with the exception of those mentioned by Wollaston, few which can be of either interest or value to the chemist of the present day, except from a purely historical point of view. From Wollaston's table onwards, I have not felt that the purposes of this paper permitted of any selection between atomic weight determinations, however valueless many of them might appear to my own judgment. Indeed, it has cost me more labor to put many ill-made and ill-reported investigations into proper form for this digest than was required for a majority of those determinations upon which I set the highest value. In the attempt to make a complete collection of the determinations since the time indicated, a few may have escaped my search; but, if so, they must have fallen singularly dead upon the chemical world, and would be unlikely to repay further labor in seek-

ing them. On the other hand, I have rigidly excluded atomic weights calculated from analyses never designed so to be used. Any chemist, upon whose experiments we could rely, would proceed in a very different manner in making an atomic weight determination, from that which he would select for an ordinary analysis, and to put his credit at stake by calculating atomic weights from analyses not designed for this use is alike unfair to him and to the scientific public, which is asked to receive as an atomic weight determination what really is not such.

The purpose of this paper is distinctly not critical, and the remarks I have added to, or inserted in, the digest are simply explanatory. I have, however, frequently mentioned criticisms which have appeared in literature when they seemed pertinent.

As for the accuracy with which the digests have been made, I may state that the preponderating importance of this point has been constantly before my mind. In the effort to crowd the maximum amount of information into the fewest words, I have had occasion to refer to most of the papers digested a number of times, and at long intervals. I have always taken advantage of such occasions, as well as those on which I have met with a reprint, translation or abstract of a determination, to verify the rough draughts of my digests. Only in a couple of instances have I thus discovered a trifling error. On the other hand, I have been able to detect and point out numerous misprints and miscalculations in the original sources. While, therefore, I cannot hope entirely to have escaped error in the thousands of values I have copied, and the almost equal number of calculations I have made, I have strong hopes that the accuracy of this digest will be found at least on a par with that of the original papers.

When, as is the case with provoking frequency, chemists have given their analytical data, but have omitted to state the atomic weights, or other constants, assumed in calculating their results, I have recalculated their data with accepted constants, which I have in each case stated. I have also, in many instances, recalculated determinations of importance,

in which constants varying considerably from those now received were assumed. I have further reduced the determinations originally given in terms of O = 100, or of O = 15.96, to O = 16. No confusion, however, will be found between the numbers for which the original investigators are responsible and my own. All values which I have calculated are in italics, or, with my explanations, enclosed in square brackets. The only arithmetical operation I have permitted myself to perform without these indications is a multiplication or division by two; and even in such cases it will usually appear from the digest itself that this operation has been performed.

The abbreviations of the literary references are essentially those adopted in the Royal Society's *Catalogue of Scientific Papers*. The first reference in each case is to the source upon which I have depended. When two references are necessary, they are connected by the word *and*. When my authority is not the original source, that to which it is accredited in my authority is also mentioned.

In conclusion, I shall be grateful to any one who, by drawing my attention to omissions or mistakes, will assist me in perfecting a labor which has occupied all my available time for twenty months.

BERKELEY, CAL., *April*, 1878.

POSTSCRIPT.

In preparing the following paper, I designed making it preliminary to a discussion of the various determinations and of the value to be assigned to each, and in this work I had already made some progress. After presenting this paper to the Institution, however, I learned that Prof. F. W. Clarke had been for some time engaged on a similar undertaking, and to him I gladly resigned the discussion of the data here compiled. The two papers will appear in the same form, and may be regarded as complementary.

G. F. B.

ATOMIC WEIGHT DETERMINATIONS.

ALUMINIUM.

The specific heat of aluminium, as determined by Regnault and by Kopp, and the vapor density of volatile compounds, as determined by Deville and Troost and by Odling, indicate that the atomic weight of this element is about 27.5. (*Gmelin-Kraut, Handbuch der Chemie*, *1*, 39; and *L. Meyer*, *Moderne Theorien der Chemie*, 50.)

J. J. Berzelius: *27.267* (O = 16).

100 parts of anhydrous aluminic sulphate decomposed by heat, gave 29.934 parts of oxide. Preparation not described. Number of experiments, probably 1. In *Berzelius' Lehrbuch* these data are calculated for S = 200.75, and give Al = 170.9 (O = 100,) or *27.344* (O = 16.) [If S = 32, the data give Al = 27.267.] (*Poggend. Ann.*, *8*, 1826, 187.*)

T. Thomson: *30* (O = 16).†

Thomson found, probably from analysis of the sulphate, (see appendix,) that 125 Al = 100 O. Thomson supposed aluminic oxide to be a protoxide. [If it is a sesqui-oxide, the data give Al at 30.] (*Thomson's System of Chemistry*, 7th ed., *1*, 1831, 454.)

W. W. Mather: 20.55 (O = 16).

According to this chemist 0.646 grammes of chloride, prepared according to Woehler, gave 2.055 grammes argen-

* This article by Berzelius, which contains the particulars of a large part of his earlier atomic weight determinations, will be referred to frequently in the course of this paper. It is unfortunately full of misprints, all of which are, by no means, corrected in the table of errata at the end of the volume. The correctly printed values of the atomic weights discussed in it are to be found in *Poggend. Ann.*, 10, 1827, 339.

† It must be remarked, in justice to Dr. Thomson, that his atomic weight determinations are, properly speaking, of a different nature from those of other chemists. So thoroughly persuaded was he of the truth of Prout's hypothesis, (that the atomic weights of the elements are all exact multiples of that of hydrogen,) that his experiments were directed merely towards ascertaining *which* multiple, in any case, was to be adopted.

tic chloride, and 0.2975 aluminic oxide. (*Silliman's Amer. Journ.*, *27* 1835, 138, 241.) Berzelius points out the inconsistency of these data. (*Berzelius' Jahresbericht*, *15*, 1835, 138.)

C. TISSIER: *27.12* (O = 16).

Determined by dissolving aluminium in chlorhydric acid, evaporating to dryness with excess of nitric acid and decomposing the nitrate by heat. The aluminium employed contained 0.135 per cent. sodium. 1.935 of this metal gave 3.645 oxide. [If Na = 23, these data give Al = 27.12.] The metal was prepared by heating aluminic fluoride with purified sodium in a graphite crucible. (*Paris Comptes Rend.*, *46*, 1858, 1105.)

J. DUMAS: 27.446 (O = 16).

Determined by six experiments on the titration of aluminic chloride with argentic nitrate. The mean result was Al = 13.723 (O=8); extreme difference 0.09. The aluminic chloride, which had been prepared on a large scale, was purified by sublimation over iron-filings and over aluminium filings, and by a third sublimation in a current of hydrogen over aluminium filings, after which it was melted. Experiments on the oxidation of aluminium were found unsatisfactory on account of the difficulty of obtaining the metal pure. They gave Al at from 13.74 to 13.89. Dumas takes Ag = 108; Cl = 35.5. (*Ann. de Chim. et de Phys.*, (3,) *55*, 1859, 151.)

W. ODLING: 27.5 (O = 16).

Determined from the vapor density of aluminium methide and ethide at 220° and upwards. (*Phil. Mag.*, (4,) *29*, 1865, 316.)

—. ISNARD: 27 (O = 16).

Pure aluminium dissolved in chlorhydric acid, evaporated and heated to redness, gives $\frac{17}{9}$ of its weight in oxide. (*Paris Comptes Rend.*, *66*, 1868, 508.)

Pelouze and Fremy give *27.357* (O = 16); 170.98 (O = 100,) for the atomic weight of aluminium, and assert that this value is derived from the composition of potash-alum, but they give no authority for the value. The experiments were made by precipitation with barium chloride. (*Traité de Chimie*, 3d ed., *1*, 50.)

ANTIMONY.

From the specific heat of antimony, as determined by Bunsen, Regnault, and others, and from the vapor density of volatile compounds, as determined by Mitscherlich, Loewig and Schweizer and others, it is certain that the atomic weight must be about 120. (*Gmelin-Kraut*, *l. c.;* and *L. Meyer*, *l. c.*)

J. J. Berzelius: *129.03* (O = 16); 806.452 (O = 100).

100 parts of pure antimony, oxidized with nitric acid, evaporated to dryness, and heated to redness, gave 124.8 antimonic antimoniate. The number of experiments and the preparation of the metal are not given. (*Poggend. Ann.*, *8*, 1826, 23.)

R. Schneider: 120.3 (O = 16); 751.9 (O = 100).

Determined by experiments on the reduction of native antimonic ter-sulphide in a current of hydrogen. The only foreign substance to be found in the mineral was silicic acid, which was determined in each case. The temperature was kept as low as possible, and the amount of sulphide volatilized, and of that undecomposed by the process, was determined. The mean composition, as ascertained by eight experiments, was 71.48 antimony—extreme difference, 0.078; and 28.52 per cent. sulphur. The atomic weight was calculated from the mean for S = 200. (*Poggend. Ann.*, *98*, 1856, 293.) Schneider published a preliminary note in *Poggend. Ann.*, *97*, 1856, 483, in which, from a portion of the above-mentioned experiments, he deduced the value 120.25.

H. Rose and Weber: *120.626* (O = 16).

Rose published this determination expressly as a confirmation of Schneider's value. Antimony ter-chloride was dissolved in water containing tartaric acid, and decomposed by hydrogen sulphide. Sulphur was removed from the filtrate by ferric sulphate, and the chlorine determined with argentic nitrate. 2.162 antimony chloride were found equivalent to 4.097 argentic chloride. [If Ag = 107.93 and Cl = 35.457, these data give Sb = 120.626; or, for O = 100, Sb = 753.92.] Rose, adopting some other values gets 1508.67 [twice 754.34.] He also recalculates some earlier

analyses of the ter-chloride, and the penta-chloride (*Poggend. Ann.*, *3*, 1825, 443) made by himself by the same method, which give respectively 1512.91 and 1508.6. (*Poggend. Ann.*, *98*, 1856, 455.)

W. P. Dexter: 122.336 (O = 16); 764.6 (O = 100).

Attempts were made to determine the atomic weight of antimony from its reducing action on the chloride of gold, but no constant result was obtained. Berzelius' method (*vide supra*) was, therefore, adopted. From the mean of ten irreproachable experiments Dexter deduces the value 1529.2; extreme difference, 3. The metal was prepared as follows: From antimony tartrate, sodium metantimonate was prepared, and antimonic acid separated out with nitric acid. The antimonic acid was reduced with carbon, and melted with another portion of antimonic acid to remove traces of sodium, etc. It was also heated in a current of hydrogen to remove traces of oxide. The investigation was carried out in Bunsen's laboratory, and with his assistance. (*Poggend. Ann.*, *100*, 1857, 563.)

J. Dumas: 122 (O = 16).

Neither the reduction of cervantite nor of the sulphide, nor the oxidation of metallic antimony gave accordant results. Dumas, therefore, resorted to the analysis of the ter-chloride with argentic nitrate. The chloride was prepared by three different methods, and was dissolved in water acidulated with tartaric acid. Seven experiments gave an average of 121.975; extreme difference, 0.69. Ag = 108; Cl = 35.5. (*Ann. de Chim. et de Phys.*, (3,) 1859, 175.)

F. Kessler: 122.24 (O = 16).

In four experiments crystals of antimony ter-oxide were employed. This oxide had been sublimed in a current of pure, dry carbonic acid. A known weight of the compound was nearly oxidized in a chlorhydric acid solution by a known, slightly insufficient, weight of potassic chlorate. The remainder was titrated with a standard solution of potassic bi-chromate, and countertitrated with ferrous chloride. The mean result was Sb = 122.16. In three experiments metallic antimony was employed. It was prepared by reducing the precipitate formed when ammonic hydrate is added to stibium-ammonium tartrate. The metal was oxidized in chlorhydric acid solution by potassic chlorate, (not weighed,) and reduced to antimony ter-chloride by

stannous chloride. The excess of this reagent was chloridized by mercuric chloride, calomel being separated by filtration. The experiment was continued exactly as in the cases where the oxide was taken to start with. The mean of the experiments on metallic antimony was 122.34. The mean of the seven experiments above described is 122.24; extreme difference, 0.94. K = 39.12; Cl = 107.97. Kessler also made experiments by Rose's method, but got discordant results. (*Poggend. Ann.*, *113*, 1861, 145.)

B. UNGER: 119.76 (O = 16).

Determined by analysis of sodium sulph-antimonate, (Schlippe's Salt.) (*Kopp's Jarresbericht*, 1871, 325; *Arch. der Pharm.*, (2,) *147*, 193; *148*, 1.) A single determination by a method from which great accuracy could not be expected. S = 32; Na = 23. (J. P. Cooke, Jr., in *Proc. Amer. Acad.*, *13*, 6.)

J. P. COOKE JR.: 120 (O = 16).

Cooke objects to the determinations of Dexter and Dumas, on the ground that there is no sufficient evidence of the absence of higher or lower compounds of the same elements in the salts employed.

In two experiments antimony was dissolved and precipitated as sulphide, which was heated to 240° before weighing. The formation of free S was prevented, occluded tartaric acid was determined, but occluded oxy-chloride was neglected. The experiments gave each Sb = 120.6 for S = 32. In thirteen experiments Sb was dissolved in a minimum of nitric acid, and the solution boiled over bullets of Sb to complete saturation. The sulphide was then precipitated in an atmosphere of carbon di-oxide. The precipitate contained no free S. The oxy-chloride was driven off at 180° and determined. The tartaric acid was decomposed at 210° and determined. The errors are opposed and minute. The mean of the weighings of sulphide, dried at 180°, gave Sb = 119.994 for S = 32; extreme difference, 1.01. The mean of weighings of sulphide heated to 210° gave Sb = 120.295; extreme difference, 1.07. General mean Sb = 120.145. Fifteen analyses of antimonious bromide gave the Br contents at 66.6665 per cent. for Ag = 108, Br = 80, with an extreme difference of 0.195. This composition gives Sb 120. In seven experiments the iodide was analyzed. For I = 127 and Ag = 108, it gave a mean of 76.051 per cent. Sb, or Sb = 120. It was also shown that the chloride

cannot be prepared free from oxy-chloride, and that its Sb and Cl contents correspond to Sb = 120. Metallic Sb was prepared by reduction of sodic antimoniate, or of oxide, with potassic cyanide, or by Liebig's method. In all cases it was fused for several hours under its own oxide. The haloid salts were purified by fractional recrystallization and distillation, in part in a current of carbon di-oxide. (*Proc. Am. Acad.*, *13*, 1877, 1.)

ARSENIC.

The specific heat of metallic arsenic, as determined by Regnault, and the vapor density of a number of volatile compounds, as determined by Dumas, Mitscherlich, Bunsen, and others, prove that the atomic weight of this element must be in the neighborhood of 75. (*Gmelin-Kraut*, *l. c.*; and *L. Meyer*, *l. c.*)

J. J. BERZELIUS: 75.1 (O = 16); 469.4 (O = 100).

2.203 grammes of arsenious acid, heated with sulphur in a distilling apparatus in such a manner that sulphurous acid, but no sulphur, could escape, set free 1.069 grammes sulphurous acid. If S = 200.75, the value follows. (*Poggend. Ann.*, *8*, 1826, 22; and *Lehrbuch*, 5 ed., *3*, 1205.)

J. DUMAS: *75* (O = 16).

Dumas found the vapor density of arsine 2.695. [This value multiplied by 28.94278 gives As = (sensibly) 75.] (*Ann. de Chim. et de Phys.*, *33*, 1826, 337.)

J. PELOUZE: *75* (O = 16); 468.75 (O = 100).

A known weight of arsenic ter-chloride was introduced into a nitric acid solution of a known weight of perfectly pure silver, the chloride being in slight excess. The excess of chloride was then titrated with decimal silver solution.* As the mean of three experiments Pelouze found As = 937.50; extreme difference, 0.8. Ag = 1349.01; Cl = 443.2. The ter-chloride was repeatedly distilled to free it from excess of chlorine. It was colorless, dissolved com-

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* This method, which has been frequently employed in the determination of atomic weights, will be referred to as "Pelouze's method."

pletely in chlorine, and boiled between 134° and 135°. (*Paris Comptes Rend.*, *20*, 1845, 1047.)

J. DUMAS: 74.94 (O = 16).

Determined by four experiments on the titration of arsenic ter-chloride with argentic nitrate, the ter-chloride being prepared in several lots. The number is the mean of the experiments; the extreme difference being 0.15. Dumas takes Ag = 108; Cl = 35.5. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 174.)

F. KESSLER: 75.2 (O = 16).

In six experiments arsenious acid was titrated with potassic bichromate and counter-titrated with ferrous chloride. The number so obtained was 75.15. In twelve experiments a known weight of arsenious acid was oxidized in caustic potash solution by potassic chlorate, the arsenious acid being slightly in excess, acidified with chlorhydric acid and the excess of arsenious acid titrated with potassic bichromate and counter-titrated with ferrous chloride. The oxidizing action of the potassic bichromate was experimentally determined. The number obtained from these experiments was 75.24. Five experiments were made with acid instead of alkaline solutions of arsenious acid; they gave 75.15. The arsenious acid was colorless, transparent, volatilized without any residue, and was thoroughly dessicated. Kessler assumed K = 39.12; Cl = 107.97. (*Poggend. Annal.*, *95*, 1855, 210; *113*, 1861, 140.)

BARIUM.

The specific heat of barium compounds, especially of the chloride, as determined by Regnault and by Kopp, shows that the atomic weight of this element lies in the neighborhood of 137. (*Gmelin-Kraut*, *l. c.*)

WOLLASTON and KLAPROTH. *139.2* (O = 16); 870 (O = 100).

Klaproth found that 100 parts of carbon di-oxide were equivalent to 352.57 parts barium oxide, and that 34 parts sulphuric anhydride were equivalent to 66 parts of barium

oxide. If C = 75.4, and S = 200, the value follows. (*Phil. Trans.*, *104*, 1814, 20.)

J. J. Berzelius: *136.79* (O = 16).

100 parts of barium chloride gave 138.08 and 138.06 parts argentic chloride. [If Ag = 107.93, and Cl = 35.457, the above value follows.] Berzelius also determined barium from the sulphate; 100 parts barium chloride gave 112.17 and 112.18 parts sulphate. Calculated for S = 200.75 this determination is almost identical with the other; Berzelius, however, expressly adopts the former. [Calculated for S = 32.0742, it gives 135.74.] (*Poggend. Annal.*, *8*, 1826, 189, and *Lehrbuch der Chemie*, 5th ed., *3*, 1229.)

E. Turner: 137.4 (O = 16).

Turner determined the chlorine contents of barium chloride at 34.016 per cent. by precipitation with silver. This number was the mean of the best two experiments made, and the value follows from it on the assumption that Cl = 35.42. The barium chloride was prepared from native carbonate by solution in chlorhydric acid, precipitation of impurities with barium oxide, ignition of the chloride, treatment with alcohol, and recrystallization. (*Phil. Trans.*, *119*, 1829, 291.*)

T. Thomson: *136* (O = 16); 850 (O = 100).

Thomson had formerly determined this atomic weight at 875 by mixing potassic sulphate with barium chloride in such proportions that the supernatant liquid contained no sensible amount of either sulphuric acid or barium. Turner having shown the fallacy of this method, Thomson substituted ammonium sulphate, and also sulphuric acid for the potassium salt, and found 9.5006 barium oxide equivalent to 5.00 sulphuric anhydride. He also analyzed the chloride with argentic nitrate, assuming silver = 1375, and chlorine = 450, and reached the same conclusion with reference to barium. (*Thomson's System of Chemistry*, 7th ed., *1*, 1831, 426.)

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* Turner made the discovery in the course of this investigation that barium sulphate carries down other salts, such as potassic sulphate, which cannot be extracted from the precipitate by any degree of washing, and that determinations, with barium sulphate, are consequently unreliable. Although Berzelius drew attention to the importance of the observation, and Thomson was obliged to acknowledge errors in his work from this cause, the fact was for a long time nearly forgotten, as can readily be proved from the contents of this digest.

—. SALVETAT: 136 ($O = 16$); 850 ($O = 100$).

Determined from the loss of weight ensuing on the decomposition of barium carbonate by sulphuric acid. Details not given. (*Paris Comptes Rendus*, *17*, 1843, 318.)

J. PELOUZE: *137.28* ($O = 16$); 858.01 ($O = 100$).

Into a nitric acid solution of a known weight of perfectly pure silver, a known and slightly more than equivalent weight of barium chloride was introduced. The excess was titrated with decimal silver solution. The value is the mean result of three experiments, which give an extreme difference of 0.22 for $O = 100$. The barium chloride was purified by recrystallizations continued till determinations gave a constant result, and was dessicated in part at 200°, and in part at a temperature just below redness. Pelouze took $Ag = 1349.01$, and $Cl = 443.2$. (*Paris Comptes Rendus*, *20*, 1845, 1047.)

C. MARIGNAC: 137.08 ($O = 16$); 856.77 ($O = 100$).

Determined by six experiments on the equivalence of silver and barium chloride performed by Pelouze's method, (*vide supra.*) 100 silver were found equivalent to 96.365 barium chloride; extreme difference, 0.038; hence the value taken. Marignac takes $Ag = 1349.01$, and $Cl = 443.2$. The barium chloride was purified as follows: Commercial chloride was crystallized from boiling aqueous solution; the crystals were heated to redness, dissolved in boiling water, treated with carbon di-oxide, filtered and crystallized, and these crystals were washed with alcohol and again recrystallized. Determinations were made at each stage and the purification was continued until constant results were obtained. (*Liebig, Annal.*, *68*, 1848, 214; *Bibl. Univ., Arch. des Sciences*, *8*, 265.)

H. STRUVE: 136.26 ($O = 16$).

100 parts of barium chloride gave 112.0938 parts of sulphate as a mean of two experiments; extreme difference, 0.005. $S = 32$; $Cl = 35.4624$. (*Liebig, Annal.*, *80*, 1851, 204; *Oefversigt af Kongl. vet. Acad. Fochr.*, *6*, 165.)

T. ANDREWS: 137.578 ($O = 16$).

Andrews obtained this number from two nearly coincident experiments of which he gives no details. (*Brit. Assoc. Rep.*, 1852, pt. 2, 33.)

C. Marignac: 137.16 (O = 16).

Three experiments were made on the titration of air-dried barium chloride in crystals by Pelouze's method, (*vide supra.*) Five grammes of the salt required for precipitation (1) 4.4205; (2) 4.4195; (3) 4.4210 grammes silver. Three experiments were made on the conversion of the same barium chloride into sulphate. Ten grammes of the salt gave (1) 9.543; (2) 9.544; (3) 9.542 grammes sulphate. In each of the latter experiments the water was determined, and was found to vary no more than 0.0005 grammes. Comparison of the two series gives for Ag = 108, S = 16, and O = 8; barium equal to (1) 68.57; (2) 68.61; (3) 68.55; in mean 68.58, or one-half of 137.16. This result is independent of the possible trace of water the chloride might have contained. In another series of three experiments the water was driven off at a low red heat and determined, and the salt analyzed by Pelouze's method. It was proved that barium chloride is not decomposed at the temperature employed. (1) gave 68.61; (2) 58.59; and (3) 68.55, or a mean of 68.583. The salt for the experiments marked (1) was prepared by recrystallization and precipitation with alcohol; that for (2) by a repetition of the same process, and for (3) by resolution of (2) and precipitation with chlorhydric acid gas. Marignac proved that the precipitated argentic chloride contained entirely insignificant traces of barium salt. Cl = 35.5. (*Bibl. Univ., Archives des Sciences, Nouv. Série.*, *1*, 1858, 209.)

J. Dumas: 137 (O = 16).

Determined by fifteen experiments on the titration of barium chloride with argentic nitrate, which give a general average of 68.516 with an extreme difference of 0.11. The barium chloride was prepared from pure nitrate and pure carbonate, and from commercially pure chloride after it had been freed from lead by precipitation with barium sulphide. The chloride was precipitated from solution by chlorhydric acid gas and melted in a current of chlorine to prevent oxidation. Ag = 108; Cl = 35.5. (*Annales de Chimie et de Physique*, (3,) *55*, 1859, 137.)

BERYLLIUM.

The atomic heat of beryllium has been determined by J. Emerson-Reynolds by direct comparison with that of silver.

In a calorimetric apparatus constructed for the purpose, the amount of heat given off during cooling by 108 parts of silver heated to 100° was found to be equal to that communicated by a little more than 9.2 parts of beryllium under the same conditions. Assuming the atomic weight of the metal to be 9.2, the atomic heat found would be 5.91. The smallness of this number the observer accounts for by supposing that there was a trace of platinum present introduced by the use of platinum vessels in the course of reduction. (*Phil. Mag.*, (5,) *3*, 1877, 38.)

J. J. BERZELIUS: *14.5* (O = 16).

Berzelius analysed the salt formed by saturating dilute sulphuric acid with beryllium oxide. From the amount of barium sulphate obtained he inferred that the atomic weight of beryllium was 331.261 on the supposition that the oxide was $Be_2 + O_3$ and that the salt was neutral. Berzelius took O = 100; S = 200.75, and Ba = 855.29. [Awdejew having discovered that this salt is basic, this value is reduced to 90.63; or, for O = 16, to 14.5.] Berzelius accepted Awdejew's determination in preference to his own. (*Poggend. Annal.*, *8*, 1826, 187; and *Lehrbuch der Chemie*, 5th ed., *3*, 1225.)

T. THOMSON: 36 (O = 16).

Experiments not given. The value is four times nine, and may have arisen from a mistake as to saturation. (*System of Chem.* 7 ed., *1*, 1831, 459.)

—. AWDEJEW: *13.85* (O = 16); *86.58* (O = 100).

Beryllium sulphate, in chlorhydric acid solution, was decomposed with barium chloride. In the filtrate the excess of barium chloride was precipitated with sulphuric acid, and the beryllium oxide thrown down with ammonia, dried, heated, and weighed. The beryllium sulphate was prepared from pure carbonate by treatment with sulphuric acid and precipitation with alcohol. It was purified by recrystallization. Four experiments were made, the mean of which calculated for S = 201.165, gave Be = 58.084 with an extreme difference of 1.955. (*Poggend. Annal.*, *56*, 1842, 106.) Weeren recalculated these analyses for S = 200 and got 57.72, [or ⅔ of 86.58.] (*Poggend. Annal.*, *92*, 1824, 124.)

J. WEEREN: *13.83* (O = 16); *86.46* (O = 100).

Weeren followed the same method as Awdejew, except that he precipitated the beryllium with ammonium sulphide, the oxide being soluble in excess of ammonia. The mean of four experiments gave 57.64, the extreme difference being 1.52 for O = 100, [57.64 is $\frac{2}{3}$ of 86.46.] Weeren took S = 200. (*Poggend. Annal.*, *92*, 1854, 124.)

G. KLATZO: *13.89* (O = 16).

Klatzo made five analyses of the sulphates containing seven and four molecules of water, precipitating the sulphuric acid as barium sulphate, and the beryllium as oxide by means of ammonia. From a comparison of the sum of the oxide found in all the analyses with the total amount of barium sulphate found, Klatzo deduces Be = 9.227, for Ba = 137, and S = 32. [If Ba is taken equal to 137.16, and S = 32.07, and if each of the analyses is calculated for itself, Be = 13.89. The extreme difference is 0.45.] The sulphates were purified by recrystallization, and treatment with alcohol. (*Erdmann's Journ. für Prak. Chemie*, *106*, 1868, 227; *Klatzo*, *Ueber die Constitution der Beryllerde*, *Dorpat*, 1868.)

L. F. Nilson and O. Pettersson have redetermined the specific heat of beryllium within a few weeks. They find the specific heat 0.4079, corresponding to a trivalent metal and a sesqui-oxide. The investigation seems to have been made with great care, while that of Emerson-Reynolds was merely preliminary. (*Berlin*, *Bericht der chem. Ges.*, *11*, 1878, 386.)

BISMUTH.

Dulong and Petit, Regnault, and Kopp, have determined the specific heat of Bismuth. It corresponds to an atomic weight of about 210. (*Gmelin-Kraut*, *l. c.*)

P. LAGERHJELM: *212.86* (O = 16); 1330.377 (O = 100).

Metallic Bismuth was oxidized in a weighed vessel by nitric acid, and the nitric acid expelled by heat. 10 grammes of bismuth gave 11.1275 oxide. (*Berzelius' Lehrbuch der Chemie*, 5th ed., *3*, 1216; *Stockholm*, *Akad. Handl.*, *34*, 1813, 219.)

R. SCHNEIDER: *208* (O = 16); 1299.98 (O = 100).

Determined by eight experiments on the conversion of metallic bismuth into oxide by solution in nitric acid and decomposition of the nitrate in the same vessel. The escaping gases were led through nitric acid, and the bismuth caught in this way was separately converted into oxide and weighed. In four experiments the bismuth was prepared by the reduction of basic nitrate, and for the other four by the reduction in hydrogen of the oxide formed in those which preceded. 100 bismuth oxide were found to contain a mean of 89.655 metal; extreme difference, 0.048. (*Poggend. Annal.*, *82*, 1851, 303.)

J. DUMAS: 210.44 (O = 16).

Determined by seven experiments on bismuth chloride, which was decomposed in solution by sodium carbonate, and the sodium chloride thus formed titrated with silver solution. The value taken is the mean result. The extreme difference is 1.12. Dumas takes Ag = 108, and Cl = 35.5. The bismuth chloride was prepared by the action of chlorine on bismuth, and was purified by fractional distillation over bismuth. That employed in the experiments was colorless. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 176.)

BORON.

The specific gravities of a number of volatile compounds of boron have been determined by Dumas, Woehler and Deville, and others, and correspond to an atomic weight of about 11. (*Gmelin-Kraut*, *l. c.*; *L. Meyer*, *l. c.*)

H. F. Weber has discovered that the specific heat of boron rises rapidly with the temperature, becoming nearly constant at 600°. Above this temperature its specific heat is 0.5, and its atomic heat 5.5. (*Poggend. Annal.*, *154*, 1875, 575.)

J. J. BERZELIUS: 11.01 (O = 16).

Davy's investigations having shown that boracic acid contains about 68 per cent. oxygen, and having thus established the formula of borax, Berzelius determined the atomic weight from the water contents of that salt. He found in three experiments, without variation, 47.1 per cent. Gmelin-Kraut recalculates this composition with Stas' atomic

weights, and gets the value given. (*Poggend. Annal.*, *8*, 1826, 19.)

-A. LAURENT: 10.86 (O = 16).

Laurent found that borax retains some water even when melted, which, however, can be expelled by the addition of iceland spar. By repeating Berzelius' experiments, and adding a known weight of spar, he found the water contents in two experiments 47.15 and 47.20. He did not regard the experiments as accurate. Gmelin-Kraut recalculates these data with Stas' atomic weights, and gets B = 10.91 and 10.81. (*Paris Comptes Rendus*, *29*, 1849, 5.)

WOEHLER and DEVILLE: 10.87 (O = 16).

These chemists titrated the bromide and the chloride of boron with argentic nitrate. They do not offer the analyses as atomic weight determinations, but Dumas applies the data to this object. Taking Ag = 108, and Cl = 35.5, Dumas calculates from the analysis of the chloride prepared by the action of H Cl on B, B = 11; from the analysis of the chloride prepared by the action of Cl on B, B = 10.6; from the analysis of the bromide prepared by the action of bromine on boron, B = 11. (*Annal. de Chimie et de Physique*, (3,) *52*, 1858, 88; *55*, 1859, 129.)

T. THOMSON: *10.67* (O = 16).

Thomson supposed boracic acid to be composed of one atom of boron and two of oxygen, and concluded from Davy's and his own experiments that the atom of B was exactly equal to that of O. For the correct composition of the acid his value must be reduced one-third. (*System of Chem.*, 7th ed., *1*, 1831, 214.)

BROMINE.

Mitscherlich determined the vapor density of bromine, and Regnault the specific heat in a solid condition at very low temperatures. Both of these constants correspond to an atomic weight of 80. (*Gmelin-Kraut*, *l. c.*; *L. Meyer*, *l. c.*)

A. J. BALARD: *75* (O = 16); 468.85 (O = 100).

1.27 potassium bromide decomposed with sulphuric acid

gave a residue of 0.973 potassic sulphate. [If this analysis is calculated with Stas' atomic weights, it gives Br = 74.65.] In another experiment 100 parts of argentic bromide reduced with zinc, the excess of which was extracted with sulphuric acid, gave 58.9 parts silver. [Calculated with Stas' data this gives Br = 75.3.] Balard mentions no special precautions in the preparation of his salts for this determination. (*Annal. de Chimie et de Physique*, *32*, 1826, 357, 362.)

J. LIEBIG: *75.29* (O = 16); 470.55 (O = 100).

2.521 potassic bromide precipitated with argentic nitrate gave 4.041 argentic bromide. The potassic bromide was obtained by adding potassic hydrate to an alcoholic solution of bromine until the solution began to lose color. (*Annal. de Chimie et de Physique*, *33*, 1826, 331.)

J. J. BERZELIUS: *78.264* (O = 16); 489.15 (O = 100).

Berzelius suspected that insufficient precautions had been taken in the preceding determinations to get rid of chlorine. He washed bromine for a long time, and converted it into zinc bromide and ammonium bromide. These salts he partially precipitated with argentic nitrate to get rid of chlorine. From the filtrate he precipitated argentic bromide which he washed, dried, and melted. 7.202 of this bromide, decomposed in a current of chlorine, yielded 5.546 argentic chloride; 7.8805 bromide gave 6.069 chloride. If Ag = 1351.607, and Cl = 442.652, the mean value of Br is as above; difference, 0.09. (*Poggend. Annal.*, *14*, 1828, 565; *Kongl. vet. Akad. Handl.*, 1828.)

C. LOEWIG: 75.76 (O = 16).

According to Gmelin-Kraut, *Handbuch der Chemie*, the determination was published in a treatise entitled *Brom und Seine Chemische Verhältnisse*, *Heidelberg*, 1829.

C. MARIGNAC: 79.957 (O = 16).

In three experiments a known weight of silver was dissolved in nitric acid, precipitated with potassium bromide, and the argentum bromide dried at 200° and weighed. [For Ag = 107.93 these experiments give Br = 79.938, with an extreme difference of 0.018.] *In vacuo* this result is, according to Stas, 79.968. In seven experiments a known weight of silver was precipitated by a determinate amount of potassic bromide by titration. [If K = 39.137, and Ag = 107.93,

this gives bromine = 79.924 with an extreme difference of 0.046.] *In vacuo* this becomes, according to Stas, 79.945. In four experiments potassium bromate was decomposed by heat, and the potassic bromide weighed. [For K = 39.137 these experiments give bromine at 80.11 with an extreme difference of 0.56. These latter are evidently much less accurate than the preceding, and I have therefore averaged the first and second series *in vacuo*.] The KBr was prepared by heating bromate purified by recrystallization. (*Berzelius' Lehrbuch der Chemie*, 5th ed., *3*, 1194; *Bibl. Univ.*, *46*, 1843, 357.)

W. Wallace: 79.74 (O = 16).

Determined by analysis of arsenic ter-bromide, by titration with argentic nitrate, according to the method of Pelouze, (see arsenic, Pelouze's determination.) Three experiments were made, giving a mean of 79.738; extreme difference, 0.051. As = 75; Ag = 107.97. The arsenic and bromine were directly combined, and the compound was purified by fractional distillation and recrystallization. (*Phil. Mag.*, (4,) *18*, 1859, 279.)

J. Dumas: 80 (O = 16).

Determined by three experiments on the conversion of argentum bromide into chloride in a current of dry chlorine. The mean is 80.03; the extreme difference is 0.18. Silver is taken at 108, and chlorine at 35.5. The argentum bromide was prepared with bromine free from iodine, and was purified from chlorine by digestion with argentum bromide. (*Annal. de Chemie et de Physique*, (3,) *55*, 1859, 162.)

J. S. Stas: 79.952 (O = 16).

Four complete syntheses (the weight of each of the constituents, and of the compound being determined) were made of argentum bromide, a known weight of silver being converted into sulphate, and precipitated with a known weight of bromine which had been converted into hydrobromic acid. The mean result was that 100 Ag = 74.0805 Br; with an extreme difference of 0.004. Two analyses of argentic bromate, made by reducing the salt in suspension with sulphurous acid, gave for the molecular weight of the bromide 187.84, and 187.90, mean 187.87. A comparison of these data gives Br = 79.940. [This, I think, must be a misprint for 79.949.] Fourteen experiments were made on the equivalence of KBr and Ag by Pelouze's method, (see

As, Pelouze's determination.) The mean result was that 100 Ag = 110.345 KBr; extreme difference, 0.029. This gives Br = 79.958 for Ag = 107.93, and K = 39.137. The bromate of silver was prepared from potassic bromate and silver salts. For the preparation of Ag see Stas' determination of it. The potassic bromate was prepared by the action of chlorine on a mixture of KBr and KHO. The bromide was prepared by the action of heat on bromate, by treating bromine with KHO, and in other ways. No reagents were probably ever prepared with such care as those employed in this and the accompanying determinations. The weights are all *in vacuo*. (*Stas, Untersuch. über Chem. Proport.*, *Leipzig*, 1867.)

CADMIUM.

Regnault, Kopp, and Bunsen have determined the specific heat of cadmium, which corresponds to an atomic weight of 112. Deville and Troost determined the density of cadmium vapor at above 1000°. It answers to an atomic weight of 114. (*Gmelin-Kraut, l. c.; L. Meyer, l. c.*)

F. STROMEYER: *111.48* (O = 16); 696.767 (O = 100).

Stromeyer found that 100 parts of cadmium combine with 14.352 parts of oxygen to form the oxide. (*Berzelius' Lehrbuch der Chemie*, 5th ed., *3*, 1219; *Schweigger's Journ.*, *22*, 1818, 362.)

T. THOMSON: *112* (O = 16); 700 (O = 100).

Thomson says that he has shown this to be the true value by analysis of the sulphate in two different states. (*System of Chem.*, 7th ed., *1*, 1831, 555.)

K. VON HAUER: 112 (O = 16); 700 (O = 100).

Determined by nine experiments on the reduction of cadmium sulphate to sulphide in a current of hydrogen sulphide under pressure. The mean of the experiments gave Cd = 55.999; extreme difference, 0.16. Von Hauer took S = 16. The sulphate was purified by repeated recrystallizations and by conversion into oxide. It was dried at 200°. The sulphide was in each case carefully examined for undecomposed sulphate. (*Erdmann's Journ. für Prak. Chem.*, *72*, 1857, 346.)

J. DUMAS: 112.24 (O = 16).

Determined by six experiments on the titration of cadmium chloride with argentic nitrate. The mean of all the experiments was Cd = 56.12; extreme difference, 0.49. The third experiment varies considerably from the rest, and Dumas seems inclined to omit it in the average. If it is left out, the mean becomes 56.06; extreme difference, 0.29. Dumas takes Cl = 35.5; Ag = 108. The cadmium chloride was prepared in two lots by solution of cadmium in chlorhydric acid, evaporation and melting for several hours in a current of chlorhydric acid gas. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 158.)

E. LENSSEN: 112.06 (O = 16).

Three experiments were made on the decomposition of cadmium oxalate, the salt and the resulting oxide being weighed. The mean result was Cd = 56.03; extreme difference, 0.19. C = 6. The oxalate was prepared from pure chloride by precipitation with oxalic acid, washing and drying at 150°. It was carefully tested, and was found to be anhydrous. (*Erdmann's Journ. für Prak. Chemie*, *79*, 1860, 281.

CÆSIUM.

The great similarity between cæsium and the other alkaline metals renders the deduction of its atomic weight from its equivalent sufficiently certain.

KIRCHHOFF and BUNSEN: 123.35 (O = 16).

Determined by three experiments on the analysis of the chloride with argentic nitrate. The value is the mean; extreme difference, 0.13. The cæsium was separated from the other alkalies by extracting a mixture of oxides and carbonates with alcohol. It was converted into chloride by precipitation with platinum chloride, reduction of the double chloride in hydrogen and solution. These operations were repeated until the cæsium salt gave sensibly the same results after successive purifications. Its purity was also tested spectroscopically. Silver was taken at 107.94, and chlorine at 35.46. (*Poggend. Annal.*, *113*, 1861, 363.)

JOHNSON and ALLEN: 133 (O = 16).

Determined by four experiments on the precipitation of cæsium chloride with argentic nitrate. The mean result was Cs = 133.036; the extreme difference, 0.842. Ag = 107.94; Cl = 35.46. Cæsium and rubidium were separated by partial crystallization of their bitartrates. The cæsium bitartrate was converted into chloride by precipitation with platinum chloride, reduction and solution. The nitrate formed on the precipitation of the cæsium chloride with silver was reconverted into cæsium chloride and redetermined, and so on. The purity of the salt was tested spectroscopically. (*Silliman's Amer. Journ.*, (2,) *35*, 1863, 96.)

R. W. BUNSEN: 133 (O = 16).

Determined by three experiments on the precipitation of cæsium chloride with argentic nitrate. The mean result was 132.99; extreme difference, 0.02. Ag = 107.94; Cl = 35.46. In order to prepare pure chloride, a mixture of cæsium and rubidium salts was converted into carbonates, a little more tartaric acid was added than was necessary to form acid tartrate with the rubidium and neutral tartrate with the cæsium, and the mixture was exposed on a filter to the action of a saturated atmosphere of aqueous vapor. The cæsium salt is deliquescent, and gradually passes through the filter, while the rubidium salt is unaffected. The cæsium tartrate was turned into pure chloride by repeated precipitation with platinum chloride, reduction in hydrogen and solution. The determinations were made on the product of successive purifications, and only those were taken into consideration which were made after analysis showed a constant composition. The spectroscope was employed to test the purity of the salt. (*Poggend. Annal.*, *119*, 1863, 5.)

—. MERCER: 133 (O = 16).

The fact of this determination, without details, is mentioned by Frankland. (*Chem. News*, *8*, 1863, 18.)

R. GODEFFROY: 132.557 (O = 16).

Derived from the mean of four analyses of cæsium chloride with argentic nitrate, the extreme difference being 0.185. Cl = 35.5; Ag = 108. The cæsium was separated from the other alkalies by the fractional crystallization of their alums continued until the cæsium compound was

spectroscopically pure. The aluminium was removed with ammonia, the sulphuric acid with barium chloride and traces of barium with ammonium carbonate. The cæsium chloride, which was not deliquescent, was dried at 150°. (*Liebig's Annal.*, *181*, 1876, 185.)

CALCIUM.

Bunsen has determined the specific heat of calcium. It corresponds to an atomic weight of 40. (*Gmelin-Kraut*, *l. c.*)

F. H. WOLLASTON: *40.736* (O = 16); 254.6 (O = 100).

Wollaston found that 43.7 parts of carbon di-oxide saturated 56.3 parts of lime. If C = 75.4, the value follows. (*Phil. Trans.*, *104*, 1814, 20.)

J. J. BERZELIUS: *40.32* (O = 16); 252.075 (O = 100).

301 parts of anhydrous calcium chloride gave 775 parts argentic chloride. If Cl = 443.28 and Ag = 1349.66 the value follows. This analysis, made in 1818, was erroneously calculated from a mistake in setting down its results and the atomic weight of Ca was taken at 256.019. (*Poggend. Annal.*, *8*, 1826, 189; and *Lehrbuch der Chemie*, 5th ed., *3*, 1227.)

J. DUMAS: 40 (O = 16).

Three experiments were made on the calcination of calcium carbonate which contained 0.03 per cent. of ferric oxide and silicic acid. The weight of the residue was in mean 56.07, or, subtracting 0.03, 56.04, with an extreme difference of 0.08. These figures give almost exactly 40. The weighings are reduced to vacuum. (*Paris Comptes Rendus*, *14*, 1842, 537.)

—. SALVETAT: 40 (O = 16); 250 (O = 100).

It is to be inferred from the context that this determination was made from the loss of weight ensuing on the decomposition of calcium carbonate by heat or sulphuric acid. (*Paris Comptes Rendus*, *17*, 1843, 318.)

C. Marignac: *40.208* (O = 16); 251.3 (O = 100).

Determined by precipitating calcium chloride with argentic nitrate; Ag = 1349.01; Cl = 443.2. Marignac laid no weight on this determination finding it impossible to prepare calcium chloride which did not show an alkaline reaction. The presence of caustic lime would make the result erroneously high; no doubt Berzelius' early analysis was defective from the same cause. (*Berzelius' Jahresbericht*, *24*, 1844, 103; *Bibl. Univ.*, *46*, 1843, 367.)

Erdmann and Marchand: 40.007 (O = 100).

Four experiments were made on the calcination of calcium carbonate enclosed in a double platinum crucible in a wind-furnace, till the weight was constant. A mean of 56 per cent. calcium oxide was found with an extreme difference of 0.05. This gives Ca = 40 for C = 12. Two experiments were made by decomposing calcium carbonate by sulphuric acid. These gave a mean of 43.99 carbonic acid; difference, 0.02. The value taken is the mean of all experiments. The carbonate was prepared by precipitating calcic chloride with ammonium carbonate, and drying at 160° to 180°. Confirmatory experiments were made on iceland spar. The weighings are reduced to vacuum. (*Erdmann's Journ. für Prak. Chem.*, *26*, 1842, 472.)

Berzelius maintained that Erdmann and Marchand employed material containing water, chlorine and magnesium. Erdmann and Marchand answered that there could be no magnesium and was no chlorine but that they had convinced themselves that spar is the only compound of certain and constant composition. Berzelius replied that they then admitted that their carbonate contained water. Erdmann and Marchand appealed to their experiments on spar, upon which Berzelius made experiments showing that spar, too, retains water at 200°. This Erdmann and Marchand denied and finally assert that all the carbonic acid is not driven off at any attainable temperature, and that their results were therefore too high instead of being too low. The error they estimate to exactly cover the difference between their averages and 40. (*Erdmann's Journ. für Prak. Chem.*, *31*, 1844, 257; *37*, 1846, 75; *50*, 1850, 237.)

Erdmann and Marchand: *40.062* (O = 16); 250.39 (O = 100).

The spar experiments referred to above. Six analyses were made as before, giving a mean of 56.028 oxide; extreme

difference 0.047. (*Erdmann's Journ. für Prak. Chemie*, *31*, 1844, 268.) Another experiment, in which the absence of water was proved, gave 56.03 lime. The weighings are reduced to vacuum. (*Erdmann's Journ. für Prak. Chem.*, *37*, 1846, 77.)

J. J. BERZELIUS: *40.264* (O = 16); 251.651 (O = 100).

Five experiments were made on the conversion of caustic lime into sulphate. The value is the mean for S = 200.75; extreme difference 0.962 for O = 100. The lime was carefully purified and burnt, but Berzelius says nothing of testing it for carbonic acid, upon which Erdmann and Marchand found an objection. Berzelius expresses himself ill satisfied with the results. (*Liebig's Annal.*, *46*, 1843, 241; also *Lehrbuch der Chemie*, 5th ed., *3*, 1228.)

J. DUMAS: 40.02 (O = 16).

Five experiments were made on the titration of calcium chloride with argentic nitrate. They give a mean of 20.065, but Dumas considers only three of them as entitled to a voice. These give 20.01; extreme difference, 0.03. The calcium chloride was prepared by dissolving marble in chlorhydric acid, digestion with lime water, filtration, evaporation, treatment with chlorhydric acid and heating in a current of chlorine. For the three experiments averaged the chloride was kept melted in the current of gas for from 8 to 10 hours. Ag = 108; Cl = 35.5. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 129.)

CARBON.

The specific gravity of gaseous carbon compounds shows that the atomic weight must be nearly 12. (*Gmelin-Kraut*, *l. c.*) Weber has shown that the specific heat of carbon at high temperatures obeys Dulong and Petit's law.

F. H. WOLLASTON: *12.064* (O = 16); 75.4 (O = 100).

Biot and Arago found the specific gravity of carbon dioxide 1.5196, and that of oxygen, 1.1036. Calculation from these data gives the value. (*Phil. Trans.*, *104*, 1814, 20.)

J. J. Berzelius: earlier determinations.

In 1817 Berzelius attempted to determine the atomic weight of carbon by two analyses of plumbic carbonate. [These analyses calculated for Pb = 206.926 (Stas,) give C = 11.998 and 11.984, or 74.99 and 74.90.] Considering the difference too great, he calculated the atomic weight from Biot and Arago's determination of the specific gravities of carbon di-oxide and oxygen, 1.10359 and 1.51961. Berzelius gives 75.33 as the result; [I make it 75.394.] Subsequently, (1819,) Berzelius and Dulong determined these specific gravities more accurately at 1.524 and 1.1026 whence he calculated C = 76.437. This number was accepted until Dumas showed it to be false, although in the mean time carbon di-oxide had been shown to be a condensible gas. According to Dumas, Berzelius at one time accepted a value 76.52 of which I have found no account. In Berzelius' *Lehrbuch*, *3*, 1174, 76.48 is a misprint for 76.437. (*Berzelius' Lehrbuch der Chemie*, 5th ed., *3*, 1197, *et passim*.)

T. Thomson: *12* (O = 16); 75 (O = 100).

Thomson found the specific gravity of carbon di-oxide 1.52673. Assuming the specific gravity of oxygen at 1.1111, chiefly to accord with the supposition that air is a compound containing 20 per cent. of oxygen, he calculates the atomic weight of carbon at 75. (*Erdmann's Journ. für Prak. Chem.*, *8*, 1836, 372; *Records of General Science, by R. D. Thomson*, 1836, 179.)

J. Dumas: about *12.16* (O = 16); 76 (O = 100).

From analysis of well crystallized naphthaline, Dumas infers that the atomic weight of carbon cannot be so high as 76.44, and must be nearly as above. (*Poggend. Annal.*, *44*, 1838, 110.)

J. J. Berzelius: *12.23* (O = 16); 76.458 (O = 100).

One experiment was made on the decomposition of plumbic carbonate by heat, which gave C = 76.405. [If Pb = 206.926, the data give C = 12.185, or 76.157.] Another experiment was made on the oxalate, which gave C = 76.511. Berzelius regards these results as confirmatory of the value 76.438. The plumbic carbonate was prepared by precipitating the nitrate with ammonium carbonate. The oxalate was obtained by decomposing the acetate with oxalic acid. (*Liebig's Annal.*, *30*, 1839, 241.)

G. Fownes: 12.12 (O = 16).

Determined by three analyses of naphthaline with cupric oxide, the usual precautions being observed. The value is the mean; extreme difference, 0.14. The naphthaline was purified by slow sublimation in a florence flask, and was brilliantly white. Fownes does not regard his results as conclusive as to the exact value. (*Phil. Mag.*, (3,) *15*, 1839, 62.)

E. Mitscherlich: *12.016* (O = 16); 75.1 (O = 100).

Experiments made on the analysis of naphthaline by the ordinary method of organic analysis gave never more than 75.2, and those which seemed most accurate very nearly 75. (*Mitscherlich's Lehrbuch der Chemie*, 4th ed., *1*, 1844, 595.)

Dumas and Stas: *12* (O = 16); 75 (O = 100).

Determined by fourteen experiments on the combustion of carbon in oxygen, the resulting carbon di-oxide being weighed. In five cases natural graphite was employed, and in four graphite from charcoal pig-iron. Both were purified by treatment with acid and heating in chlorine. The necessary oxygen was developed in the combustion-tube from potassic chlorate and cupric oxide. In five experiments diamond was employed, and the oxygen was furnished from a gasometer. The oxygen was displaced by air, especially purified from carbon di-oxide by milk of lime. The products of combustion were collected in tubes filled with pumice stone moistened with sulphuric acid, Liebig potash-bulbs and tubes filled with dry potash. The mean of the experiments on graphite gave C = 74.982; those on diamond gave 75.005; the extreme difference was 0.238. The observers point out that the result would not be affected by reduction to vacuum. (*Annal. de Chimie et de Physique*, (3,) *1*, 1841, 5.)

Liebig thinks that potash must have been volatilized, and says that there is no assurance that the oxygen was completely expelled by air. He also points out that the analyses of camphor and benzoic acid, accompanying the investigation, show an excess of carbon for C = 75. (*Liebig's Annal.*, *38*, 1841, 195.)

Erdmann and Marchand: *12.009* (O = 16); 75.054 (O = 100).

Erdmann and Marchand repeated Dumas' and Stas' experiments. Five experiments on diamond gave C = 75.028;

extreme difference, 0.38. Three experiments on natural and one on artificial graphite gave C = 75.087; extreme difference, 0.13. The number is the mean of all experiments. Erdmann and Marchand adopt 75. Calcium chloride was used in these experiments instead of sulphuric acid to avoid objections as to the possible volatility of the acid. (*Erdmann's Journ. für Prak. Chem.*, *23*, 1841, 159.)

BERZELIUS and LIEBIG and REDTENBACHER: *12.119* (O = 16); 75.741 (O = 100).

Five analyses by Berzelius of the tartrate of lead, the decomposition being effected by heat, gave 62.7431 per cent. plumbic oxide; extreme difference, 0.045. Several analyses of plumbic racemate gave a mean of 62.75 per cent. oxide; extreme difference, 0.05. The salts were prepared by fractional precipitation of plumbic acetate with tartaric and racemic acids respectively. They were dried at 100°. (*Poggend. Annal.*, *19*, 1830, 306.) From the analyses of the tartrate Liebig and Redtenbacher calculate C = 75.771, and from the racemate 75.711, taking Pb = 1294.489 and H = 6.2394. (*Liebig's Annal.*, *38*, 1841, 137.)

LIEBIG and REDTENBACHER: *12.137* (O = 16); 75.854 (O = 100).

Determined by decomposing known weights of organic salts of silver in a covered crucible by heat and weighing the silver. Five analyses of each of the following salts showed that 18.6113 Ag = 28.8098 acetate; 9.6171 Ag = 16.223 tartrate; 16.2641 Ag = 27.438 racemate; 16.0596 Ag = 25.9019 malate. If Ag = 1351.607 and H = 6.2394, the above value for C follows, with an extreme difference for the 20 analyses of 0.765, (O = 100.) The figures are all calculated for vacuum. [If Ag = 107.93 and H = 1.0025, the average number obtained from the mean of each set of analyses gives C = 12.06865 or 75.429.] The acetate was prepared by partially neutralizing pure acetic acid with ammonia, precipitating with argentic nitrate and recrystallizing the salt from hot aqueous solution. The crystals were dried at 103°. The acetic acid was prepared from plumbic acetate. The tartrate was prepared by adding tartrate of sodium and potassium to a hot (80° to 85°) dilute solution of argentic nitrate till a small permanent precipitate was formed, and cooling the solution. The racemate was prepared from pure acid racemate of ammonium like the tartrate. The malate was prepared from calcium

malate and argentic nitrate. The salt thus obtained was dissolved in nitric acid, and reprecipitated with ammonia added drop by drop, not to complete neutralization, washed and dried. (*Liebig's Annal.*, *38*, 1841, 139.)

A. Strecker recalculated Liebig and Redtenbacher's analyses given above, independently of the atomic weight of silver, from the difference in their atomic composition, employing the method of least squares. He found $C = 75.415 \pm 0.061$, or 12.066 ± 0.01. In the same way, and from the same analyses he calculated the atomic weight of silver at 1348.79, or 107.9032. [The close coincidence between this result and Stas', is certainly worthy of remark.] (*Liebig's Annal.*, *59*, 1846, 280.)

Marignac repeated Liebig and Redtenbacher's experiments and got almost the same results, but, by varying the method so as to preclude loss by spirting, different ones. (*Liebig's Annal.*, *59*, 1846, 287.)

Stas had the same experience as Marignac, and also ascribes Liebig and Redtenbacher's high results to loss by spirting. (*Bulletin de l'Acad. Roy. des Sciences de Belgique*, *16*, 1849, 9.)

C. Marignac: *11.986* (O = 16).

Determined by three analyses of the acetate of silver. The salt was decomposed by heat in a tube in such a way that the products of decomposition were forced to pass through porous silver, and loss by spirting was impossible. 100 parts of the salt were found to contain a mean of 64.664 silver, with an extreme difference of 0.005 *in vacuo*. [If $Ag = 107.93$, these figures give the above value.] Marignac regards the analysis as a confirmation of Dumas and Stas' determination. The acetate was prepared by solution of argentic carbonate in acetic acid and successive recrystallizations. (*Liebig's Annal.*, *59*, 1846, 287; *Bibl. Univ.*, *Arch. des Sciences*, *1*. 1846.)

Strecker believes that the silver in Marignac's determination must have retained carbon. (*Ibid.* 284.)

F. von Wrede: 12.019 (O = 16); 75.12 (O = 100).

Von Wrede determined the specific gravity of carbon dioxide, taking into consideration its variation from the law of Marriotte. He found it equal to $1.52037 \frac{1 + 0.0049.p.}{1 + at.}$. He also found the specific gravity of oxygen 1.1052 and

that of carbonic oxide 0.96779. Comparison gives C = 75.11 to 75.14. (*Berzelius' Jahresbericht*, *22*, 1842, 72.) Berzelius adopted this determination.

According to Gmelin-Kraut, *1*, (2,) 70, Regnault's value for the specific gravity of oxygen combined with von Wrede's for carbon di-oxide gives C = 12.0037, and with that for carbonic oxide C = 12.0105.

J. S. STAS: *12.005* (O = 16); *75.029* (O = 100).

Determined by passing carbonic oxide over a known weight of pure cupric oxide, and weighing the carbon di-oxide formed. Stas got from eight experiments C = 74.993 to 75.055. [The number taken is the mean of the results, which is misprinted in Stas' paper 75.039.] The carbonic oxide was prepared from oxalic acid by the action of sulphuric acid. It was purified from carbon di-oxide by passing through potash tubes, and from oxygen by passing over hot copper filings, and was kept in a gasometer over water, in which was dissolved a solution of stannous oxide in potash. The cupric oxide was prepared by igniting pure cupric nitrate. The carbonic acid formed in the experiments was caught in potash and sulphuric acid tubes. The amount of carbon di-oxide weighed was from 23 to 67 grammes. The weighings are reduced to vacuum. (*Bulletin de l'Acad. Roy. des Sciences de Belgique*, *16*, 1849, 9.)

GRAPHON.

B. C. BRODIE: 33 (O = 16).

By the action of potassic chlorate and nitric acid on graphite, Brodie obtained a compound of carbon, oxygen and hydrogen containing 11 atoms of carbon, and by the action of heat on this substance two others containing, respectively, 22 and 66 atoms. The first of these is analogous to the hydrated oxide of silicon obtained by Buff and Woehler, if Si = 21. From this fact, and the specific heat of graphite, Brodie concludes that the atomic weight of the graphitic form of C is 33. (*Phil. Trans.*, *149*, 1859, 249.) Graham-Otto points out that if Si = 28, graphon must be 44, and that, in that case, the argument from the specific heat loses its applicability.

CERIUM.

The specific heat of metallic cerium, as determined by W. F. Hillebrand, is 0.04479, and the atomic heat 6.18 if the atomic weight is 138. (*Poggend. Annal.*, *158*, 1876, 86.)

It is well known that cerium is always accompanied in nature by lanthanium and didymium. The former was discovered in 1839, and the latter in 1843, both by Mosander.

W. Hisinger: *137.93* (O = 16).

According to Hisinger, as reported by Berzelius, the lower oxide of cerium contains 14.821 O per 100 Ce, giving the atomic weight at 574.718 for O = 100, if the lower oxide is regarded as a protoxide. (*Poggend. Annal.*, *8*, 1826, 186.)

T. Thomson: *150* (O = 16).

Thomson analysed the sulphate and obtained for cerium the value 625, (O = 100.) [He probably took barium = 70.] (*System of Chem.*, 7th ed., *1*, 1831, 466.)

F. J. Otto: *138.91* (O = 16).

According to Gmelin, Otto found in an approximate determination Ce = 578.8, and recorded it in his revised translation of Graham's Chemistry, *1*, 1840, 222.

A. Beringer: *138.48* (O = 16).

[Three analyses of cerous chloride with silver give the atomic weight of cerium at 576.375, or 92.22, if Ag = 107.93, and Cl = 35.457. Inconsistent results are given for an analysis of the sulphide.] Three analyses of the sulphate in which the oxide was determined, gave 57.4717 per cent. so-called protoxide, [or Ce = 576.31, or 92.21, if S = 32.0742.] Analysis of the formate gave Ce = 577.04 for C = 75.85. The material for the preparations was ceric oxide obtained from cerite, and purified from lanthanium by digestion with very dilute nitric acid. The lower oxide was assumed to be Ce O. (*Liebig's Annal.*, *42*, 1842, 134.)

R. Hermann: *138* (O = 16).

The lower oxide was assumed to be Ce O. 23.523 parts of anhydrous cerous sulphate gave 29.160 parts of barium sulphate, giving Ce = 575, for O = 100, Ba = 856.88, and S = 201.16. The salt was obtained by precipitating basic

sulphate from a sulphuric solution of the cerite oxides, and converting this precipitate into the neutral salt. (*Erdmann's Journ. für Prak, Chem.*, *30*, 1843, 184.)

C. RAMMELSBERG: *137.93* (O = 16).

Hermann states that Rammelsberg experimented on cerium salts free from lanthanium, and got Ce = 574.7, the lower oxide being supposed to contain one atom of oxygen. [I cannot find the original paper.] (*Erdmann's Journ. für Prak. Chem.*, *30*, 1843, 184.)

C. MARIGNAC: *141.79* (O = 16).

The result of seven experiments on the titration of cerous sulphate, prepared from basic sulphate, with barium chloride. (*Erdmann's Journ. für Prak. Chem.*, *48*, 1849, 406; *Bibl. Univ. Arch des Sciences*, *8*, 265.) Marignac subsequently made experiments which showed these results to be too high from the impurity of the barium sulphate precipitate, (see note to Turner's determination of Barium,) and that the number 575 (for O = 100 and cerous oxide Ce O) was more probable. (*Annal. de Chimie et de Physique*, (3,) *38*, 1853, 148.)

T. KJERULF: *174.56*.

Kjerulf obtained, by three organic analyses of cerium oxalate, Ce = 727.33 on the protoxide theory, O = 100. The salt was prepared by dissolving cerium oxide in oxalic acid. (*Liebig's Annal.*, *87*, 1853, 12.) Bunsen points out that this must have been a basic salt. (*Ibid*, *105*, 1858, 50.)

R. BUNSEN and J. JEGEL: *138.192* (O = 16).

The lower oxide was presumed to contain one atom of oxygen. In two experiments cerous sulphate was decomposed with ammonium oxalate. The sulphuric acid thus liberated was determined with barium sulphate; the cerium oxalate precipitate was decomposed by heat with the formation of ceric oxide, which was weighed and the additional oxygen, introduced by heating, determined by iodometric titration. The salt was not anhydrous; the water contents was estimated by difference. The experiments gave respectively 57.49 and 57.46 per cent cerous oxide in the anhydrous salt, or Ce = 576.3 and 575.25 if S = 200. One experiment was made on hydrous cerium oxalate. The cerous oxide was found as before; the water was determined and the

oxalic acid was estimated by difference. This gave 60.02 per cent. cerous oxide, calculated for the anhydrous salt, or Ce = 575.65. The salts were prepared from cerite as follows: the mineral was digested with sulphuric acid, the sulphates formed were leached with water and with dilute nitric acid; this solution was treated with hydrogen sulphide, chlorhydric acid was added and cerium oxalate was precipitated. The oxalate was heated with magnesia to convert the cerium into the higher oxide, which was dissolved in concentrated nitric acid. After diluting the solution, chemically pure basic sulphate was precipitated. In the preparation of cerous sulphate and oxalate oxidation was prevented by the action of sulphurous acid. (*Liebig's Annal.*, *105*, 1858, 45.)

C. Rammelsberg: *138.216* (O = 16).

One experiment on the organic analysis of cerium oxalate by heating in a current of oxygen behind copper oxide gave Ce = 575.9, (O = 100,) or 92.144, (O = 16,) cerous oxide being regarded as Ce O. Rammelsberg does not adopt his own, but Hermann's determination. (*Poggend. Annal.*, *108*, 1859, 44.)

C. Wolf: *136.992* (O = 16).

Determined from experiments on the sulphate, prepared and analyzed as by Bunsen and Jegel. Wolf purified the basic sulphate by solution in nitric acid and reprecipitation in hot water, aided by recrystallizations. He found that the oftener these processes were repeated the smaller was the atomic weight resulting from the analysis. The purifications were repeated until the salt was spectroscopically free from didymium, and was perfectly white, (that employed by other investigators had been yellowish or buff.) The value taken, 45.664, [or $\frac{1}{3}$ of 136.992,] was the smallest and last value reached. The investigation was made in Bunsen's laboratory. (*Silliman's Am. Journ.*, (2,) *46*, 1868, 53.)

C. H. Wing: *137.01* (O = 16).

Two experiments were made on the decomposition of hydrous cerium sulphate with oxalic acid, the cerium oxalate being converted into ceric oxide by heat. The amount of cerous oxide in the ceric oxide was calculated according to Wolf's results, giving for the atomic weight of cerium 45.64 and 45.69, S being 32. The cerium was six times recon-

verted into basic sulphate, and repeated recrystallizations were made. The salt was white and spectroscopically pure. The determination was made in Gibbs' laboratory. (*Silliman's Amer. Journ.* (2,) *49*, 1870, 356.)

D. MENDELEJEFF: 138 (O = 16).

Mendelejeff first suggested raising the atomic weight of cerium from 92 to 138. His reasons were a specific heat determination which he had made with very impure metal, and the fact that the supposed sesquioxide had never been shown to exist. He believes that the atomic weight will be found somewhat below 138, because that is the atomic weight of barium. (*Liebig's Annal.*, suppl., *8*, 1871, 186.)

H. BUEHRIG: *140.648* (O = 16).

Determined from ten analyses of the hydrous oxalate performed by combustion in a current of pure oxygen behind copper oxide. The water was collected in tubes filled with calcic chloride, and the carbonic acid in potash. Five experiments in which the cerium oxide was not determined gave a mean of 94.1304, on the supposition that cerous oxide contains 1 atom of oxygen and that O = 15.96, with an extreme difference of 0.0445. Five determinations in which the cerium was determined as ceric oxide gave 94.2260, with an extreme difference of 0.0431. Carbon was taken at 11.97. The mean result is Ce = 94.1782 for the above mentioned assumptions, [or 140.648 for O = 16, and on the supposition that cerous oxide is a sesqui-compound.] The oxalate was prepared from basic nitrate purified by Gibbs' method of oxidation with minium and nitric acid. The salt was spectroscopically pure. (*Erdmann's Journ. für Prak. Chem.*, *120*, 1873, 222.)

CHLORINE.

The density of chlorine gas and the specific heat of chlorine compounds leave no doubt that the atomic weight of this element is nearly 35.5. (*Gmelin-Kraut*, *l. c.*)

MARCET, BERZELIUS, WOLLASTON: *35.28* (O = 16).

Marcet, by experimenting on the calcination of pure marble, and on the saturation of chlorhydric acid with lime,

found as the mean of many trials, that 50.77 calcic carbonate are equivalent to 56.1 calcic chloride. Wollaston, taking the equivalent of calcic carbonate at 630, and that of calcium at 255, calculates the equivalent of chlorine at 441 for O = 100. Wollaston cites Berzelius as having obtained the same number by the conversion of plumbic carbonate into chloride. (*Phil. Trans.*, *97*, 1807, 301; *104*, 1814, 20.)

J. J. BERZELIUS: *35.412* (O = 16); 221.327 (O = 100).

The molecular weight of potassium chloride was ascertained from four experiments on the decomposition of potassium chlorate, which on being heated lost 39.15 per cent. oxygen. This gives for the chloride 932.567, (O = 100.) 100 parts of potassium chloride were further found equivalent to 192.4 parts argentic chloride, and 100 parts of silver to 132.75 argentic chloride. The value follows. Berzelius in his *Lehrbuch* accepts Marignac's determination and ascribes the error of the value he had obtained to the imperfect decomposition of that portion of the chlorate which was carried off as dust during the experiment. (*Poggend. Annal.*, *8*, 1826, 17; also *Lehrbuch der Chemie*, *3*, 1189, 1191.)

E. TURNER: 35.42 (O = 16).

Turner made two experiments on the decomposition of plumbic chloride with argentic nitrate. Assuming the atomic weight of lead at 103.6, and that 100 silver = 132.8 chloride, these analyses gave Cl = 35.43 and 35.48. Turner also decomposed corrosive sublimate with calcic oxide neutralized with nitric acid and precipitated with argentic nitrate. If mercury = 201, these analyses give a maximum of 35.28, and a minimum of 35.21, of which Turner selects the largest. From calomel treated in the same way, he arrived at the value 35.35. From his experiments on the composition of argentic chloride (and apparently comparison with potassic chloride and chlorate) Turner got 35.45. The mean of the other experiments was 35.35, but Turner considers 35.42 as being the most likely value. The plumbum chloride was prepared from the carbonate, and was purified by recrystallization, as was also the corrosive sublimate. The calomel was "prepared by Mr. Howard," and retained traces of moisture at 300°, which would make the atomic weight derived from its analysis too small. The values are for vacuum. (*Phil. Trans.*, *123*, 1833, 529.)

F. Penny: 35.454 (O = 16).

Six experiments on the conversion of silver into nitrate gave 100 Ag = 157.441 nitrate; extreme difference, 0.028. Twelve experiments by three different methods on the conversion of silver into chloride gave 100 Ag = 132.837 chloride. Four series of experiments on the interconversion of potassic chloride, chlorate and nitrate gave for the difference between the molecular weights of the chloride and the nitrate 26.56. Corresponding experiments with sodium salts gave the same difference 26.568. The mean combined with the data for the silver salts gives the molecular weight of argentic chloride at 143.424, and Cl = 35.454. For further details see Penny's determinations of potassium, sodium, nitrogen and silver. The weighings were calculated for vacuum. (*Phil. Trans.*, *129*, 1839, 32.*)

R. Phillips: 35.688 (O = 16).

In order to avoid the error possibly incurred by the melting of argentic chloride, etc., Phillips mixed known and nearly equivalent quantities of silver dissolved in nitric acid, or of crystallized argentic nitrate, with ammonium chloride; filtered, washed, and precipitated the comparatively minute amount of chlorine in the filtrate with silver solution. The fusion of this small quantity could cause no loss of importance. Phillips confesses that his ammonium chloride was acid and the only conclusions he draws are that Cl = 36, N = 14, O = 8 and H = 1 may be taken without considerable error if silver is 108. [The method seems to have been original and is nearly that afterwards adopted by Pelouze. The acidity of the ammonium chloride would of course give Cl too high.] (*Phil. Trans.*, *129*, 1839, 35.)

C. Marignac: *36.001* (O = 16); 225.007 (O = 100).

Determined by passing chlorhydric acid gas over hot cupric oxide and condensing the water formed. The mean of three experiments was Cl = 450.013; the extreme difference is 0.2 for O = 100. The gas was made from recrys-

* This is one of the most elegant investigations of the kind to be found in chemical literature, though it scarcely receives a mention except from Stas, who accords to it the praise it deserves. Stas' wonderfully exhaustive researches were necessary to prove beyond question that chemistry has a mathematical basis, and that the atomic weights of the elements are incommensurate. Penny's investigation, taken in connection with Stas', shows that the highest degree of accuracy is not incompatible with the simplest means when they are applied with the care and acumen, without which exact results cannot, under any circumstances, be obtained.

tallized sea-salt and concentrated sulphuric acid and was dried by passing through nine tubes filled with sulphuric acid and pummice stone and with calcium chloride. The water was collected in a condenser to which drying tubes were appended. (*Paris Comptes Rendus*, *14*, 1842, 570.)

A. LAURENT: 35.468 (O = 16); 221.672 (O = 100).

Determined by three analyses of chloronaphthalintetrachloride, which he found to contain 58.22; 58.29; 58.28; per cent. Cl. The mean is 58.27 from which the value follows. (*Paris Comptes Rendus*, *14*, 1842, 456.)

According to Maumené, Laurent confessed that his salt was impure, containing chlorose compounds, in Gerhardt's *Comptes Rendus*, 1845, 108. (*Annal. de Chimie et de Physique*, (3,) *18*, 1846, 45.)

C. MARIGNAC: *35.37* (O =16); 221.07 (O = 100).

One synthesis of argentic chloride showed that 100 silver equals 32.74 chlorine. Berzelius had found 32.75, which Marignac adopts. Marignac found by six experiments on the decomposition of potassic chlorate by heat, that the molecular weight of potassic chloride was 932.14. He tested the equivalence of potassic and argentic chlorides by precipitating the former with argentic nitrate, filtering without the use of paper through a funnel with a capillary neck. The precipitate was dried and weighed, then melted and reweighed, no loss being observable. 100 potassium chloride gave 192.33 and 192.34 argentic chloride in two experiments, or reduced to vacuum, 192.26. Hence the atomic weight is 442.13. The potassic chloride was prepared by heating chlorate which had been purified by repeated recrystallizations. (*Liebig's Annal.*, *44*, 1842, 23.)

C. MARIGNAC: *35.456* (O = 16); 221.6 (O = 100).

In accordance with Pelouze's suggestion, Marignac repeated his determination of the composition of argentic chloride and of the equivalence of potassic and argentic chlorides, retaining the molecular weight of potassic chloride mentioned in the last paragraph. That value was obtained from the mean of six experiments on the decomposition of the chlorate which gave the percentage of oxygen at from 39.155 to 39.167; mean 39.161. Pelouze had got, as the mean of three experiments, 39.157. (*Paris Comptes Rendus*, *15*, 1842, 959.) Marignac made eleven experiments on the equivalence of silver and potassium chloride by Pelouze's

method, a known weight of silver being dissolved in nitric acid and added to a known and nearly equivalent amount of potassic chloride in solution, after which the excess was titrated with decimal standard solution. 100 parts of silver were precipitated by from 69.049 to 69.067, in mean by 69.062 chloride. 100 parts of chloride were precipitated by from 192.33 to 192.37, in mean by 192.348 silver. Five experiments were made on the composition of argentic chloride by dissolving silver in nitric acid, with precautions against loss by spirting, precipitation with chlorhydric acid, washing, drying, melting and weighing in the same vessel. 100 parts of silver gave from 132.825 to 132.844 chloride, mean 132.84. Calculation from these data gives *in vacuo* Ag = 1349.01; K = 488.94; Cl = 443.20; for O = 100 [or Ag = 107.921; K = 39.115; Cl = 35.456, for O = 16.] (*Berzelius' Jahresbericht*, *24*, 1844, 58; *Bibl. Univ.*, *46*, 1843, 350.)

C. Gerhardt: 36 (O =16).

By heating potassic chlorate in a current of oxygen Gerhardt got, when he took precautions against loss by spirting, a mean of 60.949 chloride, from which he deduces 36 for chlorine without giving further data. (*Paris Comptes Rendus*, *21*, 1845, 1280.) Marignac shows that no data have ever been published which, in connection with Gerhardt's experiments, would give this value for chlorine. He adds further experiments of his own which, without aiming to establish more exactly the true atomic weight, prove it less than 36 (*Liebig's Annal.*, *59*, 1846, 284; *Bibl. Univ.*, *Arch. des Sciences*, *1*, 1846.)

E. J. Maumené: *35.462* (O = 16).

Maumené made seven analyses of argentic chloride by reduction in a current of pure hydrogen. Five of these experiments were made with quantities less than 10 grammes, and gave a mean of 100 silver = 32.736 Cl. Two experiments were made with about 30 grammes each, and gave 100 silver equal to 32.86 and 32.853 chlorine. Maumené prefers the latter, and deduces from them for chlorine the value 443.67 or *35.494* taking silver according to his own experiments at 1350.32. [If silver is taken at 107.93 (Stas) the same analyses give 35.462.] (*Annal. de Chimie et de Physique.* (3,) *18*, 1846, 41.)

A. LAURENT: 35.5 (O = 16); 221.88 (O = 100).

A single experiment was made as follows: pure silver was weighed off and placed in a matrass, nitric and chlorhydric acids were added, the liquid was evaporated and the chloride melted. An empty test was carried on at the same time to act as tare. Silver was taken at 1350. (*Paris Comptes Rendus*, *20*, 1849, 5.)

J. DUMAS: 35.5 (O = 16).

Determined by chloridizing different weights of pure silver by heating the metal in a current of chlorine. Experiments on 10 grammes and 20 grammes gave a mean of 35.5055, the difference being 0.013, for chlorine, if silver is 108. (*Annal. de Chimie et de Physique*, (3.) *55*, 1859, 135.)

J. S. STAS: 35.457 (O = 16).

Stas found the atomic weight of chlorine by three independent methods:

(1.) From analysis of argentic chlorate and synthesis of argentic chloride. A known weight of the chlorate was dissolved in water, precipitated with sulphuric acid to secure advantageous division of the salt, and reduced while in suspension by a slow stream of sulphurous anhydride. The chloride was washed, dried, and weighed in the flask in which it was produced. The minute amount of chloride present in the chlorate was collected and taken into consideration, and the wash-water was carefully examined for silver. Two analyses (of about 140 and 260 grammes) gave for the molecular weight of the chloride 143.383 and 143.407, mean 143.395. A variety of syntheses of argentic chloride in the wet and in the dry way showed that 100 parts silver combined with nearly 32.850 parts chlorine. Stas assumes that none of his syntheses can possibly have given too much chloride and accepts the relation stated. These data give Cl = 35.458.

(2.) From the mutual relations of potassic chlorate and chloride and argentic chloride, combined with the composition of the last. The chlorate was decomposed either by gentle heat or in the wet way with chlorhydric acid. 100 parts of chlorate were found to contain 60.846 parts chloride as the mean of eight experiments; extreme difference, 0.012, which gives the molecular weight of potassic chloride at 74.59. The relation between potassic and argentic chloride was ascertained by Pelouze's method, (see Marignac's

determination above.) Twenty experiments on quantities of 32 grammes, and less, of silver gave 100 parts Ag = 69.103 parts KCl; extreme difference, 0.008. These data combined with the composition of argentic chloride given above, indicate for chlorine 35.460.

(3.) The composition of argentic nitrate was determined, and the difference between the atomic weights of nitrogen and chlorine. In two experiments silver was dissolved in nitric acid, the solution evaporated to dryness, and the nitrate kept melted until there was no further loss of weight. The result obtained was that 100 silver = 157.484 nitrate; difference, 0.008. From series of experiments on the relation of the chlorides of potassium, sodium, lithium and silver to the nitrates, Stas found the difference between a chloride and a nitrate from 26.586 to 26.591; mean 26.588. These data show that the atomic weight of chlorine lies between 35.455 and 35.460, and confirm the mean of all the determinations of Penny, Marignac, and Stas, 35.457. The silver for this investigation was either distilled or compared with distilled silver; it was found impossible to reduce the amount of silica in the alkaline salts below 0.002 of one per cent., it was therefore determined and allowed for; every possible method of purification by recrystallization and otherwise was resorted to to ensure purity. The weighings are all reduced to vacuum. (*Stas*, *Unters. über Chem. Proport.*, *Leipzig*, 1867.)

CHROMIUM.

The specific heat of chromium, as determined from that of the oxide by Kopp, Regnault, and Neumann, corresponds to an atomic heat of from 5.4 to 5.98, if the atomic weight is taken at 52.4. (*Gmelin-Kraut*, *l. c.*)

J. J. Berzelius: *56.29* (O = 16); 351.819 (O = 100).

100 parts of plumbic nitrate, on precipitation with potassic chromate, gave 98.772 parts plumbic chromate. The value follows for Pb = 1294.498, and N = 88.518. (*Poggend. Annal.*, *8*, 1826, 22.)

T. Thomson: *64* (O = 16); 400 (O = 100).

3.14 grains of metallic chromium, converted into chromic acid by heating with potash and nitre, gave a precipitate of 16.23 grains plumbic chromate. (*Phil. Trans.*, *117*, 1827, 159.)

E. PELIGOT: *52.48* (O = 16); 328 (O = 100).

Peligot reached this value by a careful carbon determination of chromous acetate, produced by precipitating a dilute solution of chromium protochloride with sodium acetate, C = 75. Peligot does not regard the experiment as definitive, the salt possessing but little stability. (*Annal. de Chimie et de Physique*, (3,) *12*, 1844, 527.)

N. J. BERLIN: *52.54* (O = 16); 328.39 (O = 100).

Five experiments were made on the decomposition of argentic chromate with chlorhydric acid and alcohol. The silver chloride was washed in the flask in which it was precipitated, treated with aqua regia, melted and weighed without removal. The decanted fluid and the wash-water were evaporated to dryness with excess of ammonia, treated with water and the chromium oxide filtered off, heated to redness and weighed. [Nothing is said of the recovery of any argentic chloride that might have been removed by the decantation.] The value taken is calculated from the comparison of the amounts of argentic chloride and of chromium oxide obtained, Ag = 1349.66; Cl = 443.28. The extreme difference is 1, for O = 100. The argentic chromate was prepared by adding nitrate to a solution of potassic chromate. (*Erdmann's Journ. für Prak. Chem.*, *38*, 1846, 145.)

V. A. JACQUELIN: *50.08* (O = 16); 313 (O = 100).

By washing and purifying violet chromium chloride, Jacquelain obtained a substance which he took to be the pure chloride and which was more soluble than the unpurified salt. He analysed it by melting with soda, and arrived at the above number. (*Liebig's Annal.*, *64*, 1847, 275; *Revue Scient.*, *14*, 198.)

A. MOBERG: *53.563* (O = 16); 334.769 (O = 100).

Moberg made twelve experiments on the decomposition of chromium salts by heat. In two cases the sulphate dried at a low red heat was decomposed by strong ignition in a platinum crucible; the results being, 335.65 and 335.29 for chromium. Ten experiments were made on the decomposition of ammonium-chromium-alum which had been dried in a pulverized state for a long time. These determinations gave from 333.965 to 335.739. The value taken is the mean. The alum employed was prepared from pure material, and was repeatedly recrystallized. S = 200; N = 87.5. (*Erdmann's Journ. für Prak. Chem.*, *43*, 1848, 115.)

J. Lefort : *52.97* (O = 16).

Determined by fourteen experiments on the precipitation of barium with sulphuric acid from a nitric acid solution of barium chromate. The barium chromate was prepared by precipitating potassium chromate with barium nitrate and drying the precipitate at 250°. [If these analyses are calculated for barium = 137 and S = 32, they give 100 barium chromate = 60.244 barium oxide, extreme difference, 0.26, and the atomic weight as above. Lefort seems to have taken Ba = 136.72. Berlin points out the correction which I have verified.] (*Erdmann's Journ. für Prak. Chem.*, *51*, 1850, 261 ; *Journ. de Pharm. et de Chim.*, *18*, 27.)

R. Wildenstein : *53.485* (O = 16).

Determined by thirty-two experiments on the precipitation of barium chloride, desiccated at a red heat, by pure, neutral potassic chromate. The mean of these analyses gave 100 barium chromate = 81.70 barium chloride ; extreme difference 0.35. Wildenstein calculates 334.48 without giving the assumption for chlorine. [If Cl = 35.457 ; Ba = 137, the value follows.] (*Erdmann's Journ. für Prak. Chem.*, *59*, 1853, 28.)

F. Kessler : 52.3 (O = 16).

Kessler reached this value by comparing the oxidizing action of potassic chromate with that of potassic chlorate on arsenious acid. Six experiments were made on the oxidizing power of the chromate and twelve on that of the chlorate by a method of titration. By combining the maximum of one with the minimum of the other series, Kessler finds the atomic weight of chromium between 25.93 and 26.40 ; in mean 26.15, K being = 39.12 and Cl = 35.45. Confirmatory experiments were made on the oxidation of ferrous chloride in the same way. These gave a mean of 26.1. (*Poggend. Annal.*, *113*, 1861, 137 ; *95*, 1855, 208.)

M. Siewart : 52.094 (O = 16).

Determined from the amount of chlorine in sublimed violet chromium chloride. Siewart criticises Kessler's determination and deduces from the latter's data a value 25.02. (*Kopp's Jahresbericht*, *14*, 1861, 240 ; *Halle*, *Zeitschr. für die Gesammt. Naturwis.*, *17*, 530.)

Kessler points out that the number 25.02 is a misprint in the *Jahresbericht*, and that Siewart's paper ascribes to him the value 26.02. (*Poggend. Ann.*, *117*, 1862, 352.)

COBALT.

The atomic heat of cobalt as determined by Regnault is 6.27 if the atomic weight is assumed at 58.8. (*Gmelin-Kraut, l. c.*)

E. ROTHOFF: *58.98* (O = 16); 368.65 (O = 100).

269.2 parts of cobalt oxide converted into neutral cobaltous chloride and precipitated with argentic nitrate gave 1029.9 argentic chloride, according to Berzelius' report. (*Poggend. Annal.*, *8*, 1826, 185.) Berzelius recalculates this analysis for Cl = 221.64 and Ag = 1349.66, and gets the value taken. (*Berzelius' Lehrbuch*, *3*, 1220.)

R. SCHNEIDER: 60.006 (O = 16); 375.04 (O = 100).

Determined from four analyses of the oxalate. The carbon was determined as in organic analysis; the metal by heating a known weight of the salt first in a current of air, then in one of oxygen, and by reduction of the oxide in hydrogen. The mean of the four analyses gave cobalt at 30.003, with an extreme difference of 0.026 for C = 6. The oxalate was prepared by converting the chemically pure cobalt of commerce into roseo-cobaltic chloride, from which the metal was again reduced, then dissolved in chlorhydric acid and carbonate precipitated, which was digested with oxalic acid. (*Poggend. Annal.*, *101*, 1857, 398.)

Marignac objects to this determination that the oxalate, being insoluble, may very likely have retained portions of the carbonate which could not be removed by washing. (*Bibl. Univ., Arch. des Sciences*, (2,) *1*, 1858, 372.)

Schneider answers that he obtained nearly identical results from lots prepared at different times, and that he believes that he has convinced himself that the oxalate contained no carbonate. (*Poggend. Annal.*, *107*, 1859, 610.)

Gibbs, reporting Schneider's determination, remarks: "Very numerous and carefully made analyses of the ammonium-cobalt bases, executed in my laboratory, indicate 29.5 as the true equivalent of cobalt." (*Silliman's Amer. Journ.*, (2,) *25*, 1858, 438.)

C. MARIGNAC: about 59 (O = 16).

Five experiments were made on the decomposition of cobalt sulphate by heat. This salt can be readily dried without decomposition, and the acid is completely driven off by heat, but the resulting protoxide contains a slight

excess of oxygen. In order to remove this excess it was melted under a known weight of an acid silicate of lead. The results for cobalt varied from 29.32 to 29.38. The sulphate was purified by recrystallization. Marignac also experimented on the chloride. The weight of this salt varies greatly with the moisture of the atmosphere when crystallized, and attempts to desiccate it usually result in the formation of some insoluble compound. Three analyses of chloride appearing to contain one molecule of water, and dried at 100°, performed by titration with silver solution, gave cobalt at 29.42 to 29.51. Five experiments were made in the same way on chloride either melted in a current of chlorine or of chlorhydric acid gas, or calcined with ammonium chloride. These determinations gave from 29.36 to 29.42. (*Bibl. Univ., Arch. des Sciences*, (2,) *1*, 1858, 374.) [Marignac, in another investigation in the same volume, takes Ag = 108; Cl = 35.5.]

J. Dumas: 59 (O = 16).

Determined by five experiments on the titration of cobalt chloride with silver. The mean result for cobalt was 29.542; extreme difference 0.09; Ag = 108; Cl = 35.5. The chloride was prepared by dissolving pure cobalt in aqua regia, evaporating in the presence of excess of chlorhydric acid and heating to redness in a current of chlorhydric acid gas. In two of the determinations cobalt from a different lot, which had been heated in a vacuum was employed. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 148.)

W. J. Russell: 58.74 (O = 16).

Determined by fifteen experiments on the reduction of cobalt oxide in hydrogen. The value is the mean; the extreme difference is 0.19. To obtain pure cobalt oxide Claudet's salt was prepared, purified by recrystallization, etc., reduced in hydrogen, the metal dissolved in nitric acid and the resulting salt decomposed by heating in a stream of carbon di-oxide. (*Chem. Soc. Journ.*, (2,) *1*, 1863, 57.)

Schneider considers that no sufficient precautions were taken to exclude air in these experiments, and that higher oxides were formed. (*Poggend. Annal.*, *130*, 1867, 310.)

E. von Sommaruga: 60 (O = 16).

Determined by seven experiments on the reduction of purpureocobaltic chloride in a current of hydrogen. The mean of the experiments is 29.965; four of them give a

mean 29.996. The extreme difference is 0.093. The salt was prepared by solution of the carbonate in chlorhydric acid, addition of ammonia in excess, exposure to the air, washing of the precipitate with acidulated, then with pure water and drying at 110°. A special examination showed it free from other metals. Sommaruga took $Cl = 35.5$; $N = 14$. (*Erdmann's Journ. für Prak. Chem.*, *100*, 1867, 113; *Sitz.-Bericht der k. k. Akad.*, 1866.)

C. Winkler: 59 ($O = 16$).

This value is derived from the mean of five experiments on the precipitation of gold from a solution of neutral crystallized chloride of gold and sodium. The metallic cobalt employed was prepared by the reduction of purpureo-cobaltic chloride. The latter was made from oxide, and was purified by recrystallization. Gold was assumed at 196. The mean of the results was 29.496; extreme difference, 0.071. (*Fresenius' Zeitschr. für Anal. Chem.*, *6*, 1867, 22.)

P. Welesky: 58.98 ($O = 16$).

Determined from the analysis of cobalti-cyanides, performed by drying the salt at 100°, and heating to redness, first in a current of oxygen then of hydrogen. Four experiments with phenylammonium-cobalti-cyanide gave cobalt at from 29.38 to 29.59. Two experiments with ammonium-cobalti-cyanide gave from 29.46 to 29.55. Mean, 29.48; extreme difference, 0.21. A single experiment by Winkler's method gave 29.42. (*Berlin, Bericht der Chem. Ges.*, *2*, 1869, 592.)

W. J. Russel: 58.76 ($O = 16$).

Determined by the amount of hydrogen set free by the solution of cobalt in hydrochloric acid. The value is the mean of 2 (or 4?) trials. The cobalt employed was that reduced by Russel in his former experiments on the same atomic weight. (*Chem. News*, *20*, 1869, 20.)

R. H. Lee: 59.10 ($O = 16$).

Determined by analysis of cobalti-cyanide salts. They were decomposed in a crucible by heating from above. The carbon separated was burned off in air and then in oxygen, and the metallic oxide reduced in hydrogen. Six experiments on the strychnine salt gave a mean of 59.05. Six experiments on the brucine salt gave 59.15. Six experi-

ments, made with especial care, on the reduction of purpureo-cobaltic chloride by hydrogen gave 59.09. (Reported by Gibbs. *Berlin, Bericht der Chem. Ges.*, *4*, 1871, 789.)

COPPER.

Regnault, Kopp, and others have determined the specific heat of copper. It corresponds to an atomic heat of about 6 if the atomic weight is taken at 63.3. (*Gmelin-Kraut, l. c.*)

R. CHENEVIX: F. H. WOLLASTON: *64* (O = 16); 400 (O = 100.)

Chenevix found 20 parts of oxygen equivalent to 100 parts of copper, whence Wollaston deduces the atomic weight. (*Phil. Trans.*, *104*, 1814, 21.)

J. J. BERZELIUS: *63.296* (O = 16); 395.6 (O = 100).

Determined by two experiments on the reduction of cupric oxide with hydrogen, which gave 395.695 and 395.507. The water was not weighed. (*Poggend. Annal.*, *8*, 1826, 182; and *Lehrbuch*, *3*, 1216.)

ERDMANN and MARCHAND: 63.456 (O = 16); 396.6 (O = 100.)

Determined by four experiments on the reduction of large quantities of cupric oxide in a current of hydrogen. The hydrogen was displaced by air after the completion of the reduction. The weight of the oxide and of the copper were reduced to vacuum, but not that of the weights employed. To obtain pure cupric oxide, pure vitrol was prepared and electrolytically decomposed. The copper thus obtained was dissolved in nitric acid, and the nitrate decomposed by heat. The value is the mean; the extreme difference is 0.056 for O = 8, or 0.112 for O = 16. (*Erdm. Journ. für Prak. Chem.*, *31*, 1844, 389.)

Berzelius points out that these analyses vary among themselves much more than his own. He makes the difference somewhat greater than it really is by neglecting the reduction to vacuum. (*Ibid.*, *37*, 1846, 72.)

Hampe shows that these analyses, correctly calculated, give Cu = 63.46. (*Zeitschr. für Berg Hütten-und-Sal- Wesen im Preus. St.*, *21*, 1873, 261.)

J. Dumas: 63.5 (O = 16).

Dumas says that experiments on the reduction of cupric oxide and on the sulphidation of copper have shown him that the atomic weight of copper lies between 31.5 and 32, near 31.75, but that his experiments cannot be regarded as decisive. (*Annal. de Chimie et de Physique*, (3,) *55*, 1859, 129.)

Millon and Commaille: 63.128 (O = 16); 394.55 (O = 100).

These (three) experiments were in most respects a repetition of Erdmann and Marchand's. The value is the mean; the extreme difference is 0.49 for O = 100, or 0.0784 for O = 16. The sulphate was prepared free from iron or zinc by dissolving copper in ammoniacal sulphate or nitrate. The oxide was obtained by heating the nitrate. (*Paris Comptes Rendus*, *56*, 1863, 1249; and *57*, 1863, 145.)

Fresenius sees no reason for preferring this to Erdmann and Marchand's value. (*Fresenius' Zeitschr. für Anal. Chem.*, *2*, 1863, 474.)

W. Hampe: 63.3296 (O = 16).

In three experiments cupric oxide was reduced in a current of hydrogen with all possible precautions. The hydrogen was displaced by air before weighing, though it was shown by experiment that porous copper does not condense hydrogen. The metal was heated till incipient melting was observed. The reduction and melting were repeated without altering the weight. Hampe attempted to control his results by reconverting the metal into oxide, but was unable to effect complete oxidation. The water produced by the reduction was found to be perfectly pure. The mean result was Cu = 31.6696, maximum, 31.6729, minimum, 31.6648. The oxide was prepared from metallic copper. To obtain pure metallic copper, sulphate free from bismuth was electrolytically decomposed, the finely divided metal well washed, then melted, first in a current of carbon di-oxide, afterwards in hydrogen, and then again in carbon di-oxide. From the metal, basic nitrate was formed and from this salt, by heating first in air and then in oxygen, oxide. In two experiments the atomic weight of copper was determined by decomposing cupric sulphate by electrolysis, and weighing the metal. The residual fluid was evaporated, and a minute amount of copper, which had escaped decomposition, was

recovered and determined as sulphide. For S = 16.037 and O = 8, these experiments gave Cu = 31.6577 and 31.66. The value taken is the mean of the two series. All weighings were reduced to vacuum. (*Zeitschr. für Berg Hütten- und Sal.-Wesen im Preus. St.*, *21*, 1873, 260.)

DIDYMIUM.

W. F. Hillebrand found the specific heat of this metal 0.04563, which corresponds to an atomic heat of 6.60 for an atomic weight of 144.78. (*Poggend. Annal.*, *158*, 1876, 78.)

C. Marignac: *148.8* (O = 16); *930* (O = 100).

Determined by decomposing disulphate with barium chloride. Assuming the lower oxide as a prot-oxide, he calculated the atomic weight at 620. As Marignac was not confident of the purity of his salt, and subsequently became certain that the method was untrustworthy, details are unnecessary. (*Liebig's Annal.*, *71*, 1849, 313.)

C. Marignac: *143.81* (O = 16); *898.8* (O = 100).

Five experiments were made on the sulphate by decomposition with ammonium oxalate. The didymium oxalate was heated to redness, and the resulting oxide weighed. On the assumption that the oxide was protoxide, these determinations gave a mean of 598.2 for Di, with an extreme difference of 2.5. Three experiments were made on the chloride, the insoluble oxychloride, which is unavoidable in drying the salt, being separated. The chlorine was determined with silver, and the Di as in the previous experiments. These determinations gave Di at 600.2, with an extreme difference of 5.2 for Cl = 443.2 and S = 200. The salts were prepared from cerite. The cerium was extracted by treatment at first with dilute and afterwards with concentrated nitric acid. The sulphates of Di and La were separated by partial precipitation with oxalic acid and by partial recrystallization. (*Annal. de Chimie et de Phys.*, (3,) *38*, 1853, 148.)

R. Hermann: *142.44* (O = 16); *890.25* (O = 100).

In one experiment sulphate which had been heated to a low red heat, was dissolved, decomposed with ammonium

oxalate, the precipitate incinerated and the oxide weighed. The result was Di = 594.46, on the prot-oxide hypothesis, for S = 200. In one experiment the chloride was decomposed with argentic nitrate, oxychloride being filtered off and allowed for, and the argentic chloride weighed. This experiment gave Di = 592.54 for Cl = 443.2. For the preparation of the salt see Lanthanium. (*Erdmann's Journ. für Prak. Chem.*, *82*, 1861, 387.)

II. Zschiesche: About *144* (O = 16).

In five experiments the sulphate was exposed to a white heat until the weight became constant and the oxide on being tested showed no traces of sulphur. The results varied from Di = 46.585 to 48.08, probably, Zschiesche thinks, on account of the presence of La. S =16. Di was separated from La by the partial precipitation of the nitrates with oxalic acid, the first portion falling being redissolved, and the partial precipitation repeated twenty times. (*Erdmann's Journ. für Prak. Chem.*, *107*, 1869, 74.

C. Erk: *142.695* (O = 16).

The sulphate was decomposed with ammonium oxalate, the oxalate incinerated and the oxide weighed. The sulphuric acid was also precipitated as barium salt, and weighed. Three experiments gave a mean of Di = 95.13, on the prot-oxide hypothesis, with an extreme difference of 0.78. The Di salt was found to contain yttrium which was removed by repeated fractional precipitation with sodium sulphate. This re-agent precipitates a double salt of Di and sodium. The purification was continued until the atomic weight became constant. (*Kopp's Jahresbericht*, 1870, 319, *Jena'sche Zeitschr, für Med. und Nat.*, *6*, 299.)

Casselmann thinks that the salt may still have retained yttrium, and Fresenius objects to the barium sulphate determination on the well-known grounds. (*Fresenius' Zeitschr*, *10*, 510.)

D. Mendelejeff: 138 (O = 16).

From the analogy between Di and cerium and other elements, and from the fact that it forms two oxides, Mendelejeff believes that its lower oxide is a sesqui-oxide, and its atomic weight 138. Mendelejeff points out that an error is to be apprehended in the received values from the fact that we have no guarantee of the pureness of Di salts except recrystallization. (*Liebig's Annal. Suppl. 8*, 1871, 190.)

P. T. Cleve: 147.01 ($O = 16$).

Determined by the conversion of didymium oxide into sulphate. The number is the mean of six experiments; extreme difference 0.58. The Di was separated from lanthanium by repeated precipitations of basic nitrate from nitric acid solution, conversion into formate and decomposition of this salt by heat. (*Kopp's Jahresbericht*, 1874, 259. *Bulletin Soc. Chimique*, (2,) *21*, 246.)

W. F. Hillebrand: 144.78 ($O = 16$).

Determined by one experiment on the conversion of metallic Di into nitrate, and then, by heat, into oxide. The impurities were determined. The metal was reduced electrolytically from the chloride. (*Poggend. Annal.*, *158*, 1876, 78.)

ERBIUM.

The physical and chemical analogies of the salts of this element have led Mendelejeff (*Liebig's Annal., Suppl. 8*, 1871, 195,) and P. T. Cleve (*Kopp's Jahresbericht*, 1874, 260; *Bulletin Soc. Chimique*, (2,) *21*, 344,) to regard it as triatomic, and its atomic weight as about 170.

M. Delafontaine: *113.04* ($O = 16$).

M. Delafontaine investigated gadolinite by Mosander's method, and obtained besides yttrium, two substances which he regarded as erbium and terbium. From the sulphates, in which he supposed the metals to exist as protoxides, he determined erbium at 496 and terbium at 471 for $O = 100$. Popp (*Liebig's Annalen*, *131*, 189,) and Bunsen and Bahr (*Ibid*, *137*, 1,) have shown that Mosander's method gives only mixtures. Delafontaine's terbium is thought to have been chiefly the erbium of other chemists. (*Liebig's Annal.*, *134*, 1865, 108.)

Bahr and Bunsen: *168.9* ($O = 16$).

A known weight of erbium oxide was treated with a very slightly excessive quantity of sulphuric acid; the solution evaporated and the excess of acid driven off at as low a temperature as possible. The increase of weight indicates 112.6 for $S = 32$. The oxide was prepared from gadoli-

nite. The mineral was decomposed with chlorhydric acid, and the earths precipitated with oxalic acid. The oxalates were converted into nitrates, the cerium metals separated with potassic sulphate, and calcium and magnesium with ammonia. If the nitrates of yttrium and erbium are dissolved in boiling water, basic erbium nitrate with some yttrium crystallizes out, leaving yttrium nitrate with some erbium in solution. The process of partial crystallization was continued as long as the atomic weight of the erbium salt continued increasing. Bahr and Bunsen believe, however, that the atomic weight may be some hundredths higher. The salt was spectroscopically free from didymium. (*Liebig's Annal.*, *137*, 1866, 2.)

P. T. Cleve and O. M. Hoeglund: *170.55* (O = 16).

Determined from four syntheses of the sulphate, giving 113.7 on the diatomic hypothesis. The oxide was purified by heating the nitrates, etc., according to Berlin. (*Blomstrand* in *Berlin, Ber. der Chem. Ges.*, 1873, 1467; *Bull. Soc. Chimique*, 1873, 193 and 289.)

FLUORINE.

Dumas and Peligot and others have determined the vapor-density of a number of fluorine compounds. They correspond to an atomic weight of about 19. (*L. Meyer*, *l. c.*)

H. Davy: *18.86* (O = 16).

Determined by the conversion of Derbyshire spar into sulphate. 100 parts of spar gave a maximum of 175.2 parts calcic sulphate. [If S = 32; Ca = 40; the value follows.] (*Phil. Trans.*, *104*, 1814, 64.)

J. J. Berzelius: *18.85* (O = 16).

Determined by conversion of calcic fluoride into sulphate. 100 parts fluoride gave, in mean of three experiments, 175 parts sulphate: extreme difference, 0.2. [If S = 32; Ca = 40; the value follows.] (*Poggend. Annal.*, *8*, 1826, 18, and *Lehrbuch*, *3*, 1196.)

P. Louyet: 19 (O = 16).

Determined by six experiments on the conversion of fluor-spar into calcic sulphate. The mean result was 100 parts spar equal 174.36 sulphate, with an extreme difference of 0.3. Spar from Derbyshire was pulverized, digested with chlorhydric acid, and the foreign matter removed by lutration in water. It was completely dissolved in sulphuric acid, the excess of which was driven off by heat continued till a constant weight was obtained. S = 200; Ca = 250. (*Erdmann's Journ. für Prak. Chem.*, *47*, 1849, 104; *Annal. de Chim. et de Phys.*, (3,) *25*, 1849, 291.)

E. Fremy.

This chemist says that his analyses essentially confirm Berzelius' determination. (*Annal. de Chimie et de Phys.*, (3,) *47*, 1856, 27.)

J. Dumas: 19 (O = 16).

Determined by the conversion of fluorides into sulphates. A single experiment on the conversion of calcic fluoride gave 18.96; two experiments on sodic fluoride, 19.06; and two on potassic fluoride, 18.99. The mean is 19.01; extreme difference, 0.12. Ca = 20; Na = 23; K = 39; S = 16. The alkaline salts were well crystallized and were fused before use. (*Annal. de Chim. et de Phys.*, (3,) *55*, 170.)

S. de Lucca: 18.96 (O = 16).

Determined by four experiments on the conversion of a pure spar from Gerfalco into sulphate. The extreme difference was 0.15. The decomposition was very difficult. The loss on ignition and the residue left on evaporation of the acid employed were taken into consideration. [S apparently = 16; Ca = 20.] (*Paris Comptes Rendus*, *51*, 1860, 299.)

GALLIUM.

Berthelot has determined the specific heat of gallium at 0.079 corresponding to an atomic heat of 5.52, if the atomic weight is 69.9. (*Paris Comptes Rend.*, *86*, 1878, 786.)

L. DE BOISBAUDRAN: 69.9 (O = 16).

This chemist "has prepared several chlorides, [*samples* of chloride?] several bromides, and several anhydrous iodides of gallium. He has determined the atomic weight of gallium, and found it 69.9, (mean of two experiments.)" (*Paris Comptes Rend.*, *86*, 1878, 756.)

GOLD.

Dulong and Petit and Regnault have determined the specific heat of gold. It corresponds to an atomic weight of about 200. (*Gmelin-Kraut*, *l. c.*)

J. J. BERZELIUS: *196.4* (O = 16).

Determined by the amount of mercury necessary to precipitate a known weight of gold from solution of chloride. 142.9 mercury were found equivalent to 93.55 gold. [If Hg = 200, this gives Au = 196.397.] (*Poggend. Annal.*, *8*, 1826, 178.)

T. THOMSON: 200 (O = 16).

This value is derived from a somewhat inaccurate experiment on the reduction of auric chloride by ferrous sulphate. (*Edinb. Trans. Roy. Soc.*, *11*, 1831, 26.)

J. J. BERZELIUS: *196.73* (O = 16).

Determined by five experiments on the relative amount of gold and of potassic chloride in the residue obtained by heating the double chloride of the two metals in an atmosphere of hydrogen. [Calculated for KCl = 74.594, (Stas,) these experiments give a maximum of 196.79, minimum of 196.63 and a mean of 196.727. The atomic weight derived from the first experiment is misprinted in the Lehrbuch, as is the mean in the Jahresbericht.] (*Berzelius' Jahresbericht*, *25*, 1846, 41; and *Lehrbuch*, *3*, 1845, 1212.)

A. LEVOL: *196.26* (O = 16).

A known weight of gold was converted into chloride, and this salt decomposed in boiling solution by a current of pure, washed sulphurous acid. The sulphuric acid formed

was precipitated as barium salt, and the atomic weight calculated by comparison of the gold employed and the barium sulphate obtained. 1000 gold gave 1782 sulphate. [If the atomic weight of S = 32.0742, and that of Ba = 137.08, the above value follows.] (*Annal. de Chimie et de Phys.*, (3,) *30*, 1850, 355.)

HYDROGEN.

The density of hydrogen as determined by a great number of investigators, especially Regnault, is about $\frac{1}{16}$ of that of oxygen. If oxygen is 16, the atomic weight of hydrogen is consequently about 1.

The atomic weights of the elements are compared either with that of oxygen or with that of hydrogen. The main advantage of assuming hydrogen as unity is the simplicity of the approximate values expressed in terms of the atomic weight of this element. The hypothesis of Prout has also had much influence in giving currency to this unit. The advantages of oxygen as a standard of comparison consist in the fact that it combines with all the elements, except fluorine, and in the superior accuracy of the determination of its specific gravity. The percentage variation between Regnault's determinations of the specific gravity of hydrogen was thirty-six times as great as occurred in his experiments on oxygen. Unnecessary complication in the approximate values of the atomic weights is as well avoided by assuming oxygen at 16 as by taking hydrogen at 1.

These reasons for the adoption of the atomic weight of oxygen as a standard of comparison appear to me conclusive, and accordingly all values in this paper have been reduced to O = 16.

F. H. WOLLASTON: *1.06* (O = 16); 6.64 (O = 100).

Gay-Lussac and Humboldt having shown that two volumes of hydrogen and one of oxygen form water, and Biot and Arago having determined the specific gravity of these gases, Wollaston calculated the above atomic weight. (*Phil. Trans.*, *104*, 1814, 20.)

BERZELIUS and DULONG: *0.9984* (O = 16); 6.24 (O = 100).

Determined by three experiments on the reduction of cupric oxide by hydrogen. The hydrogen was made from

pure materials, and passed through a solution of litharge in potash, and over a coarse powder of caustic potash before use. The resultant water was caught in calcic chloride and weighed. The determination was also confirmed by experiments on the specific gravity of oxygen and hydrogen. The minimum result for hydrogen was 0.9934, the maximum 1.0086. (*Thomson's Annals of Phil.*, *2*, 1821, 48.)

T. THOMSON: *1* (O = 16); 6.25 (O = 100).

Thomson found the Sp. Gr. of H = 0.0694. Taking that of O as 1.1111 on theoretical grounds (the supposed compound nature of air, etc.,) he calculates the above value. (*Erdmann's Journ. für Prak. Chem.*, *8*, 1836, 374; *Records of Gen. Sci.*, *R. D. Thomson*, 1836, 179.)

J. DUMAS: *1.0012* (O = 16); 6.2575 (O = 100).

Determined by nineteen experiments on the reduction of cupric oxide with pure hydrogen. The gas was made from pure materials and was passed through solutions of plumbic nitrate and argentic sulphate, and over potash, and dried with cold sulphuric acid or with phosphoric acid. The weighings of the oxide and of the reduced copper were made *in vacuo*. [Dumas corrected the results obtained for the air contained in the sulphuric acid, but does not explain how he estimated it, while certain other possible corrections are not mentioned.] The mean of the corrected results is 12.515. The extreme difference is 0.09 for O = 100. Without the correction for absorbed air the mean is 12.533, [or 1.00264]; maximum 12.583; minimum 12.481. (*Paris Comptes Rend.*, *14*, 1842, 537.)

ERDMANN and MARCHAND: *1.0016* (O = 16); 6.26 (O = 100).

Determined by eight experiments on the reduction of cupric oxide with hydrogen, the number is the mean of the results. In four of the experiments the correction for vacuum was calculated. These gave H = 12.548; extreme difference, 0.067. In four experiments the weighings were made *in vacuo*. These gave a mean of 12.492, with an extreme difference of 0.015. The oxide employed was either copper scale or was produced from cupric nitrate. The hydrogen was made from pure zinc and sulphuric acid, and was purified with potash in solution and in lumps, mercuric chloride, sulphuric acid, and chloride of calcium. In the

last five experiments the gas was also passed over red-hot copper to remove traces of oxygen.) (*Erdmann's Journ. für Prak. Chem.*, *26*, 1842, 461.)

J. S. STAS: 1.0025 (O = 16).

From all the investigations that have been made on the specific gravity of the gases, the composition of water, etc., Stas is inclined to believe that the atomic weight of hydrogen cannot be less than above. Stas found that 100 silver were equivalent to 49.5973 ammonium chloride. [If N = 14.044, and Cl = 35.457, this relation would give H = 1.0074.] (*Stas, Untersuch. über. Chem. Prop., Leipzig*, 1867.)

J. THOMSEN: *1.0025* (O = 16).

Thomsen made three experiments on the oxidation of a known volume of hydrogen by cupric oxide, and five experiments on the combustion of a known volume of hydrogen in oxygen, which proved that 2 litres of hydrogen gave 1.6082 grammes of water under normal conditions, and at latitude 45°. According to Regnault, 1 litre of oxygen and 2 litres of hydrogen would weigh 1.6084 grammes. Hence 1 volume oxygen and 2 volumes hydrogen form water; and if H = 1, O = 15.96, [or if O = 16, H = 1.0025.] (*Berlin, Ber. der Chem. Ges.*, *3*, 1870, 928.)

INDIUM.

Bunsen found the specific heat of In 0.565 and 0.574, which correspond to an atomic weight of about 114. (*Poggend. Annal.*, *141*, 28.)

F. REICH and T. RICHTER: *111.39* (O = 16).

In one experiment pure indium was dissolved in nitric acid, the oxide precipitated with ammonia and weighed. This experiment gave In = 463.4 for O = 100, and on the supposition that the metal was di-atomic. In a second experiment indium sulphide was dissolved in nitric acid, and the resulting sulphuric acid precipitated with barium chloride. This gave In = 464.9. The number taken is the mean. S = 200. The metal was prepared from the oxide. After the removal of lead, etc., with hydrogen sulphide, the oxides

of iron and indium were precipitated with ammonia, the precipitate dissolved in acetic acid and impure indium sulphide reprecipitated. This operation was repeated, and the last traces of iron were removed by partial precipitation with ammonia. (*Erdmann's Journ. für Prak. Chem.*, *92*, 1864, 484.)

C. Winkler: *107.754* (O = 16).

Determined by decomposing the nitrate by heat, and weighing the resulting oxide. The mean result of three experiments was In = 35.918 for O = 8, and assuming the univalence of the metal. Extreme difference, 0.079. Metallic indium was prepared by solution of the impure sulphide in chlorhydric acid, precipitation of indium by barium carbonate, solution in sulphuric acid, and precipitation by ammonia of the oxide which was reduced by hydrogen. [This indium seems to have contained iron.] (*Erdmann's Journ. für Prak. Chem.*, *94*, 1865, 1.)

C. Winkler: *113.439* (O = 16).

In two experiments the double chloride of gold and sodium was decomposed by pure indium, giving 37.73 and 37.80 for O = 8, and assuming univalence for the metal. In two experiments the nitrate was decomposed by heat, giving In = 37.845 and 37.879. In one experiment the oxide was precipitated from nitric acid solution by ammonia. This experiment gave In = 37.811. The number taken is the mean. The impure indium sulphide was purified as in Winkler's former determination with barium carbonate, but this process requires to be repeated several times. The reduction of the oxide was performed with sodium, the excess of which was removed from the regulus by cupellation in soda. (*Erdmann's Journ. für Prak. Chem.*, *102*, 1867, 282.)

R. Bunsen: 113.76 (O = 16).

Determined by converting metallic indium into oxide by means of nitric acid and heat. He seems to regard the experiment only as confirmatory of Winkler's. The metal was the same which served for the determination of the specific heat, and was carefully tested for all impurities. (*Poggend. Annal.*, *141*, 1870, 28.)

IODINE.

Dumas determined the specific gravity of iodine vapor. It answers to an atomic weight of about 127. (*Annal. de Chim. et de Phys.*, *33*, 1826, 337.)

L. J. Gay-Lussac: *123.9* (O = 16).

100 parts of iodine were found equivalent to 26.225 parts of zinc. [If Zn = 65, these figures give the atomic weight at 123.9.] (*Poggend. Annal.*, *14*, 1828, 559; *Annal. de Chimie*, *91*, 1814, 5.)

W. Prout: *126* (O = 16).

Prout found 100 parts of iodine equivalent to 25.8 parts of zinc. [If Zn = 65, this gives I = 125.97.] (*Thomson's Annals of Phil.*, *6*, 1815, 323.)

T. Thomson: *124* (O = 16); 775 (O = 100).

Thomson found 20.5 potassic iodide $\doteq$ 19.75 zinc iodide, = 20.75 plumbic nitrate. [If K = 39.1, and plumbic nitrate = 331, the relation given leads to an atomic weight of 124.41.] Thomson thinks that his iodine may have been somewhat impure, as he purified it only by sublimation. (*Thomson's System of Chem.*, 7th ed., *1*, 1831, 81.)

J. Dumas: *126.13* (O = 16).

Dumas determined the density of iodine vapor at 8.716 for air = 1. [Referred to the molecular weight of oxygen, this density gives the above number for the atomic weight.] Dumas thinks it probable that it can be more accurately determined by analysis. (*Annal. de Chim. et de Phys.*, *33*, 1826, 337.)

J. J. Berzelius: *126.26* (O = 16); 789.14 (O = 100).

Determined by decomposing a known weight of argentic iodide in a current of chlorine, melting the chloride and expelling free chlorine by atmospheric air. The number is the mean of two experiments; difference, 0.01. Ag = 1351.607; Cl = 442.653. The iodide was prepared by precipitation from a solution of potassic iodide with argentic nitrate. The first portion of the precipitate was set aside as possibly contaminated with chlorine. (*Poggend. Ann.*, *14*, 1828, 562.)

C. Marignac: 126.844 (O = 16).

In five experiments a known weight of silver was dissolved in nitric acid and precipitated by a known amount of potassic iodide according to Pelouze's modification of Gay-Lussac's method. The mean result was 100 Ag = 153.74 KI in air; extreme difference, 0.14. Stas has recalculated this result for Ag = 107.93, and K = 39.137. The atomic weight so found is, *in vacuo*, 126.847. In three experiments a known weight of silver was dissolved and precipitated as iodide; mean result, 100 Ag = 217.511 iodide. Extreme difference, 0.04. From these data Stas gets I = 126.84. The iodine was purified by recrystallization as potassic iodate. The methods employed by previous experimenters were ineffectual. (*Berzelius' Jahresbericht*, *24*, 75; *Bibl. Univ. de Genève*, *46*, 1842, 367; also, *Stas, Untersuch. über Chem. Prop.*, 153.)

E. Millon: *126.07* (O = 16); 787.915 (O = 100).

Three experiments were made on the decomposition of potassic iodate. The mean loss of oxygen was 22.473 per cent; extreme difference, 0.03. If K = 488.94, this gives I = 1580.93. In three experiments argentic iodate, which had been dried for a long time at 200°, was employed, which lost 17.0467 per cent. oxygen; extreme difference, 0.03. If Ag = 1349.01, these data give I = 1570.73. [Berzelius cites this as an atomic weight determination; Millon, however, seems to have regarded it only as a confirmation of Berzelius' number.] Millon prepared pure iodine by passing a current of chlorine through a solution of KI till the precipitated I was redissolved, and reprecipitating with an excess of KI. (*Annal. de Chim. et de Phys.*, (3,) *9*, 1843, 407.)

V. A. Jacquelin: 125.6 (O = 16); 785 (O = 100).

Determined by the analysis of iodic acid with silver. The acid was prepared by the oxidation of iodine with nitric acid of sp. gr. 1.5. The purity of the preparation does not seem to have been tested. Ag = 1351. (*Erdmann's Journ. für Prak. Chem.*, *51*, 1850, 458; *Annal. de Chim. et de Phys.*, (3,) *30*, 1850, 332.)

J. Dumas: 127 (O = 16).

Determined by the conversion of argentic iodide into chloride in a current of dry chlorine. Two experiments gave 127.04 and 127.01 for Ag = 108; Cl = 35.5. In Gmelin-Kraut's *Handbuch* these data are recalculated for Ag =

107.93 and $Cl = 35.457$, giving $I = 126.941$ and 126.928. The argentic iodide used was prepared from zinc iodide which had been prepared from iodine in large crystals. The argentic iodide was fused. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 163.)

J. S. STAS: 126.851.

Stas ascertained the molecular weight of argentic iodide as follows:

In two complete analyses, a known weight of argentic iodate was decomposed by heat in a current of pure, dry nitrogen. The oxygen set free was caught by hot copper and weighed, as well as the residual argentic iodide. In one experiment argentic iodate was dissolved in ammonia, precipitated by sulphuric acid, (to secure advantageous division of the salt,) and reduced while in suspension by a slow current of sulphurous acid. The mean molecular weight reached was 234.779; extreme difference, 0.063. The samples of iodate employed were prepared: (1.) From argentic sulphate and potassic iodate, mixed boiling, the latter in excess, thorough washing and drying in air freed from organic particles; (2.) By the reaction of potassic iodate on argentic hyposulphite. The purity of the salt was carefully tested.

Stas ascertained the composition of argentic iodide as follows:

(1.) A known weight of argentic nitrate was precipitated by hydro-iodic acid and the argentic iodide washed, dried, and weighed in the same vessel. (2.) A known weight of Ag was dissolved in nitric acid, converted into sulphate, dissolved in very dilute sulphuric acid, and precipitated with hydro-iodic acid. The precipitate was washed at temperatures increasing up to 90°. (3.) A known weight of argentic sulphate was allowed to react on a known and nearly equivalent weight of iodine in an aqueous solution of sulphurous and sulphuric acids at 10°, and in the dark, till all the iodine was taken up. The excess of iodine was titrated with silver solution, and the iodide weighed. This method was employed in two experiments. (4) differed from (3) mainly in the conversion of the iodine into ammonium iodide before bringing it into contact with argentic sulphate. Four experiments were made by the last method.

The mean composition of the iodide, as derived from all the experiments, is 100 Ag = 117.5343 iodine. From these data Stas calculates the atomic weight of I at 126.857, and

that of silver at 107.928. [The sum of these weights is not the molecular weight, and this, as well as recalculation of the data, shows that the number is a misprint for 126.851. Stas' results are, therefore, even closer to Marignac's than his memoir would indicate.]

Most of the experiments were made with iodine prepared by the decomposition of nitric iodide decomposed in a large volume of water at 65°. The iodine was further purified by distillation over barium oxide and by other means. For the preparation of silver see that metal. All possible precautions were observed in the preparation of all reagents and in the conduct of the experiments. (*Stas*, *Untersuch. über Chem. Prop. Leipzig*, 1867.)

IRIDIUM.

Regnault determined the specific heat of iridium. It corresponds to an atomic weight of about 198. (*Gmelin-Kraut*, *l. c.*)

J. J. BERZELIUS: *197.19* (O = 16).

Berzelius determined this value from analysis of potassium chloro-iridiate. This salt reduced in hydrogen lost 29 per cent., the same quantity lost by the corresponding platinum salt, (*vide* platinum.) Berzelius originally calculated the atomic weight of the platinum metals both from the loss of chlorine of these double salts and from the relation between the metal and the potassic chloride left after reduction. In his *Lehrbuch* he points out the impossibility of complete desiccation, and resorts exclusively to the latter method of calculation. With respect to iridium he merely asserts that its atomic weight is the same as that of platinum, without there, or elsewhere, giving data as to the amounts of iridium and potassic chloride found in the reduced salt. It is, therefore, open to question whether he assumed the identity from the loss on reduction or not. [If Pt = Ir, and if KCl = 74.594, the value follows; see platinum.] Osmium and iridium were separated by fusion with nitre, solution, and distillation. The residue was fused with potassic chloride and sodium carbonate. On solution the iridium remains behind. This residue was repeatedly roasted and reduced to drive off osmium compounds. The potassium chloro-iridiate was formed from the pure metal. (*Poggend. Ann.*, *13*, 1828, 468; *Kongl. Vet. Acad. Handl.*, 1828.)

C. E. CLAUS: W. M. WATTS: 197.6 (O = 16).

Watts recalculated two analyses of potassium chloroiridiate by Claus from the loss in reduction, and for Cl = 35.457, (Stas.) From one analysis he finds K = 39.87, and Ir = 198.56; from the other K = 39.93, and Ir = 196.62. (*Chem. News*, *19*, 1869, 302.)

IRON.

Regnault, Kopp and others have determined the specific heat of this metal. It corresponds to an atomic weight of about 56. (*Gmelin-Kraut*, *l. c.*)

L. J. THENARD: F. H. WOLLASTON: *55.2* (O = 16); 345 (O = 100).

Thenard determined the composition of the oxide at 22.5 O and 77.5 Fe, whence Wollaston calculates the value. (*Phil. Trans.*, *104*, 1814, 21.)

J. J. BERZELIUS: *54.27* (O = 16); 339.213 (O = 100).

Determined by repeated experiments on the oxidation of iron, such as is used for piano wire, with nitric acid. The carbon was determined and allowed for. Berzelius in his *Lehrbuch* shows that the error in this determination lay in the unsuspected presence of soluble silica and on reäitnalysis he found enough of it to correct the number when taken into account. (*Poggend. Ann.*, *8*, 1826, 185.)

G. MAGNUS: *54.25* (O = 16); *339.06* (O = 100).

Magnus' experiments were made by reducing ferric oxide in a current of hydrogen at about the temperature of boiling mercury. He regarded them simply as comfirmatory of Berzelius' number. (*Poggend. Ann.*, *3*, 1825, 84.)

F. STROMEYER: *55.6* (O = 16).

Determined by reducing ferric oxide at a red heat by hydrogen. The oxide is reduced only with great difficulty at a lower temperature. The mean of the experiments gave the oxygen contents at 30.15 per cent., [whence I have calculated the value.] (*Poggend. Ann.*, *6*, 1826, 475.)

H. Capitaine: *51.36* (O = 16); 321 (O = 100).

Determined by the peroxidation of galvanically reduced iron and by measuring the hydrogen evolved on the solution of iron in sulphuric acid. (*Annal. de Chim. et de Phys.*, (3,) *2*, 1841, 126.)

H. Wackenroder: *55.48* (O = 16).

Wackenroder helped Stromeyer in his reduction of ferric oxide, of which he gives the details. He also describes five experiments of his own, which gave the oxygen contents of ferric oxide at from 30.01 to 30.38. He took no precautions to purify his hydrogen and thinks that the loss of oxygen may have been apparently reduced. [30.195 oxygen corresponds to the above value for Fe.] (*Berzelius' Jahresbericht*, *24*, 1844, 121; *Archiv. der Pharm.*, *36*, 1844, 22.)

Svanberg and Norlin: *55.97* (O = 16); 349.809 (O = 100).

In seven experiments a known weight of iron was dissolved in nitric acid and the salt decomposed by heat. The operation was performed in a glass flask. The mean result *in vacuo*, was 349.104; extreme difference, 0.803. In seven experiments ferric oxide was reduced with purified hydrogen. The mean was Fe = 350.514; extreme difference, 0.735. The number taken is the mean of all the experiments, *in vacuo*. Berzelius in his *Lehrbuch* cites the experiments and, by neglecting the reduction to vacuum, gets a slightly different number. He also expresses a preference for the experiments by reduction. (*Berzelius' Jahresbericht*, *24*, 1844, 121; and *Poggend. Ann.*, *62*, 1844, 270.)

J. J. Berzelius: *56.05* (O = 16); 350.32 (O = 100).

Berzelius, as a check on the last determination, made two experiments on the oxidation of iron by nitric acid with special precautions against partial reduction. The number is the mean; difference, 0.101. The iron was melted down with glass and magnetic oxide. In his *Lehrbuch* he adopts the mean of these experiments and Svanberg and Norlin's reduction determinations. (*Poggend. Ann.*, *62*, 1844, 270.)

Erdmann and Marchand: *56.016* (O = 16); 350.1 (O = 100).

Erdmann and Marchand made eight experiments on the reduction of ferric oxide in a carefully purified current of

hydrogen. The weighings of the metal were made *in vacuo* to avoid possible reoxidation in displacing the gas by air. The number is the mean of the experiments; extreme difference, 1.4 for O = 100. The ferric oxide was prepared by incineration of the oxalate, moistening the residue with nitric acid and reheating. (*Erdmann's Journ. für Prak. Chem.*, *33*, 1844, 1.)

L. E. Rivot: *54.25* (O = 16); 339.01 (O = 100).

Determined by two experiments on the reduction of pure ferric oxide in a current of hydrogen. 100 parts of oxide gave 69.31 and 69.35 parts metallic iron. (*Annal. de Chim. et de Phys.*, (3,) *30*, 1850, 188.)

E. Maumené: *56.0016* (O = 16); 350.01 (O = 100).

Maumené made six experiments by dissolving iron wire in aqua regia, precipitating with ammonia, heating the precipitate to redness and weighing. The number is the mean; extreme difference, 0.34. Maumené had convinced himself by analysis of the extreme purity of the wire. (*Erdmann's Journ. für Prak. Chem.*, *51*, 1850, 350.)

J. Dumas: 56.2 (O = 16).

Two experiments on the precipitation of ferric chloride by argentic nitrate gave each 28.1. A single experiment by the same method on ferrous chloride which was slightly yellow, gave 28.1. An experiment made on ferrous chloride, which had been heated in a current of hydrogen and of HCl and was colorless, but contained metallic iron, gave when the admixture was determined, 27.99. Dumas takes Ag = 108; Cl = 35.5. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 157.)

LANTHANIUM.

W. F. Hillebrand has determined the specific heat of metallic lanthanium. It corresponds to an atomic heat of 6.23, if the atomic weight is taken at 139. (*Poggend. Ann.*, *158*, 1876, 82.)

Several investigations on the atomic weight of lanthanium were made previous to Mosander's announcement of the discovery of didymium. F. J. Otto found it *108.41* shortly after its discovery, and announced it in his translation of

Graham's chemistry. (*Gmelin's Handbuch*, 5th ed., *1*, 46.) Choubine, from analysis of the chloride and of the sulphate, arrived at *108.45*. (*Erdmann's Journ. für Prak. Chem.*, *26*, 1842, 443.) Rammelsberg determined it from the sulphate, which was rose-colored, at *133.17*. (*Poggend. Ann.*, *55*, 1842, 65.) R. Hermann found La = *144* from rose-colored sulphate. (*Erdmann's Journ. für Prak. Chem.*, *30*, 1843, 198.)

C. G. MOSANDER: *139.2* (O = 16); *870* (O = 100).

Mosander says that his experiments show the true value to be in the neighborhood of 680, (the metal being assumed bivalent,) but that his salts were not pure, and the determination of little value. (*Poggend. Ann.*, *60*, 1843, 301.)

C. MARIGNAC: *141.12* (O = 16); *882* (O = 100).

Eleven experiments were made on the decomposition of the sulphate by barium chloride. The results vary greatly. Marignac wrote later (*Annal. de Chim et de Phys.*, (3,) *38*, 1853, 148) that experiment had convinced him of the incorrectness of this determination, and that the true value is about 575. (La bivalent.) (*Liebig's Ann.*, *71*, 1849, 306.)

M. HOLZMANN: *139.22* (O = 16); *870.15* (O = 100).

In three experiments La sulphate was decomposed by ammonium oxalate. In the filtrate from the precipitated oxalate the sulphuric acid was determined as barium salt. The oxalate was decomposed by heat, and the lanthanium oxide weighed. These experiments gave a mean of 580; extreme difference, 5.6; for bivalent lanthanium. In three experiments the iodate was decomposed by oxalic acid, the oxide determined as before, and the iodine titrated by Bunsen's method. These experiments gave a mean of 580.2; extreme difference, 5.3. S = 200; Ba = 855. In the preparation of the salts analyzed the cerium was separated by peroxidation with magnesium oxide and precipitation as basic sulphate. After the removal of yttrium by potassic sulphate, the lanthanium and didymium salts were separated, by making a saturated solution of the sulphates at a temperature of three or four degrees, and gradually raising the temperature. Lanthanium salt then crystallizes out nearly pure. The purification was repeated until the salts were not discolored when heated in an open crucible over the glass-blower's lamp. Bunsen assisted at this investigation. (*Erdmann's Journ. für Prak. Chem.*, *75*, 1858, 343.)

C. Czudnowicz: *140.3* (O = 16); *876* (O = 100).

Czudnowicz especially disclaims making this as an atomic weight determination and he adopts Holzmann's value. The salt analysed was the sulphate, and the method the same as that employed by Holzmann. (*Erdmann's Journ. für Prak. Chem.*, *80*, 1860, 31.)

R. Hermann: *139.32* (O = 16); *870.75* (O = 100).

Hermann analyzed the carbonate by decomposing it over mercury by sulphuric acid, and measuring the carbon dioxide liberated. The residue was heated to redness and weighed. This experiment gave La = 580.4, the metal being assumed as bivalent. The carbonate was prepared by precipitating the sulphate with sodium bicarbonate. In three experiments the sulphate was decomposed by ammonium oxalate and the oxide, obtained by incinerating the oxalate, weighed. These analyses gave La = 580.7. In one experiment the chloride was analysed with argentic nitrate, giving La = 580.4. The number taken is the mean; extreme difference 2.3. In the preparation of the salts, cerium was separated as basic sulphate, La and didymium were partially separated by crystallization after which a portion of the nearly pure sulphate was precipitated by ammonia, and this precipitate digested with the mother liquor. Didymium sulphate is by this means completely precipitated. S = 200; Cl = 443.2; C = 75. Hermann remarks that his former determination was made with impure material. (*Erdmann's Journ. für Prak. Chem.*, *82*, 1861, 395.)

H. Zschiesche: *135.27* (O = 16).

Determined by six experiments on the sulphate. The water was driven off at 230°, and the anhydrous salt exposed to a white heat until the weight became constant, and on being tested, showed no sulphur. The mean result was La = 45.09; extreme difference, 1.15. In preparing the salt from cerite, the cerium was peroxidized with red lead and nitric acid and was precipitated as basic nitrate. The didymium was separated by partial precipitation with oxalic acid and concentration, these operations being repeated as long as the absorption lines of Di were perceptible in the spectroscope. A correction was made for the loss of weight of the crucible, and there was no dust upon its sides. S = 16. (*Erdmann's Journ. für Prak. Chem.*, *104*, 1868, 174; *107*, 1869, 72.)

C. Erk: *135.39* (O = 16).

Determined by analysis of the sulphate by the method employed by Holzmann. The bases were separated by the methods which Hermann used. Yttrium was also eliminated. Fresenius in his *Zeitschrift*, *10*, 509, objects to the details of the Erk's manipulation of barium sulphate. (*Kopp's Jahresbericht*, 1870, 319; *Jena Zeitschr. für Med. und Nat.*, *6*, 1870, 299.)

D. Mendelejeff: 180 (O = 16).

As La forms but one oxide, the salts of which are not, according to Marignac, isomorphous with those of the lower oxide of didymium, Mendelejeff concludes that it belongs to the same group, but that its oxide is a binoxide, and its atomic weight 180. (*Liebig's Ann.*, *Suppl.*, *8*, 1871, 190.)

C. Marignac: *138.75* (O = 16).

By heating the sulphate till all acid was expelled, Marignac, in two experiments, determined La (bivalent) at 92.52 and 92.56; by precipitation with ammonia and heating at 92.24 and 92.48. The sulphate was purified by a great number of partial recrystallizations, and showed only doubtful traces of didymium in the spectroscope. S = 16. (*Annal. de Chim. et de Phys.*, (4,) *30*, 1873, 67.)

P. T. Cleve: 139.15 (O = 16).

Determined by the conversion of lanthanium oxide into sulphate. The number is the mean; extreme difference 0.55. The oxide was purified from didymium by repeated partial precipitation from nitric acid solution with ammonia, basic didymium nitrate going down. The lanthanium was finally precipitated with oxalic acid. The oxide was found to be spectroscopically pure by Thalén. (*Kopp's Jahresbericht*, 1874, 257; *Paris Bull. de la Soc. Chim.*, *21*, 196, 246, 344.)

LEAD.

Regnault, Kopp and others have determined the specific heat of lead. It answers to an atomic weight of about 207. (*Gmelin-Kraut*, *l. c.*)

J. J. Berzelius and F. H. Wollaston: *207.4* (O = 16); 1295 (O = 100).

Berzelius found 16.5 parts carbon di-oxide equal to 83.5 lead oxide, whence the value, if C = 75.4. [If C = 12, these figures give lead at 206.67.] Berzelius also determined the composition of the oxide at 7.15 oxygen and 92.85 lead, giving Pb = *207.52* or 1297. (*Phil. Trans.*, *104*, 1814, 20.)

J. J. Berzelius: *207.12* (O = 16); 1294.498 (O = 100).

Determined by the reduction of a known weight of oxide of lead by hydrogen and the weight of the resultant lead; mean of four nearly coincident experiments. (*Poggend. Ann.*, *8*, 1826, 184.

— Longchamp is credited in some books with an atomic weight determination of lead. He made none, but only speculated on the composition of minium, taking Berzelius' determination as a basis. (*Annal. de Chim. et de Phys.*, *34*, 1827, 105.)

J. J. Berzelius: *207.078* (O = 16); *1294.242* (O = 100).

This value is the mean of six experiments on the reduction of the oxide in a current of hydrogen. The oxide was produced by the decomposition of the nitrate by heat. As this compound reacts upon Pt, the crucible was lined out with a coating of a very basic nitrate, which prevented the lumps of neutral salt from coming in contact with the crucible. The glass in which the oxide was reduced was not attacked. [The third analysis is miscalculated. It should show an atomic weight of 1295.595. The mean is, therefore, as above, and the extreme difference 2.421.] (*Poggend. Ann.*, *19*, 1830, 314.)

J. J. Berzelius: *207.14* (O = 16); 1294.645 (O = 100).

In his *Lehrbuch*, Berzelius selects five analyses made by the above method, three of them the same. These give the above mean, with an extreme difference of 0.704 for O = 100. (*Lehrbuch*, *3*, 1219.)

E. Turner: *207.3* (O = 16).

Determined by experiments on the conversion of metallic lead and of oxide of lead into the sulphate by solution in

nitric acid and evaporation with sulphuric acid. In three experiments, Turner found 100 lead = 146.401 sulphate; extreme difference 0.055. Berzelius had found 100 Pb = 146.419 sulphate; extreme difference 0.078. Turner takes the mean of his own and Berzelius' determinations, 146.41. In one experiment Turner found 100 oxide = 135.92 sulphate. Combination of these results gives Pb = 103.6 [or more accurately 103.65.] The oxide was prepared from subnitrate. The lead was prepared from plumbic acetate which was converted into carbonate, then into nitrate, in which form it was recrystallized, then again into carbonate, and reduced by black flux. On testing, it was found perfectly pure. Weighings reduced to vacuum. (*Phil. Trans.*, *123*, 1833, 524.)

C. Marignac: 207.04 (O = 16).

Marignac made four experiments on plumbic chloride by Pelouze's modification of the silver titration method. He found Pb = 103.57–.49–.55–.46. The number taken is the mean. The salt was titrated cold, argentic chloride being soluble in hot solutions of plumbic nitrate. The plumbic chloride was purified by recrystallization, and, after being pulverized, was dried at about 200°. According to Marignac there is no difficulty in desiccating it completely at this temperature. Ag = 108; Cl = 35.5. Marignac found it impossible to convert the chloride into the sulphate completely. (*Bibl. Univ., Arch. des Sciences*, (2,) *1*, 1858, 223.)

J. Dumas: 207.1 (O = 16).

From a single experiment on the precipitation of the chloride with argentic nitrate. The chloride used was heated for twelve hours in a current of dry HCl, and the amount of water retained determined. Dumas found it impossible entirely to desiccate the salt without decomposition, drying at 250° does not desiccate it. Cl = 35.5; Ag = 108. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

J. S. Stas: 206.926 (O = 16).

According to the mean of 10 syntheses of plumbic nitrate, 100 lead = 159.9703 nitrate; extreme difference, 0.023. If N = 14.044, this relation gives Pb = 206.918. Stas also made six syntheses of the sulphate, which gave in mean 100 Pb = 146.4275 sulphate; extreme difference, 0.024. If S = 32.0742, this relation gives Pb = 206.934. The syntheses were made in the same way as in the determination of the

atomic weight of silver. The drying of the nitrate could be accomplished only *in vacuo* and at about 155°. The weighings are for vacuum. The lead used was prepared from commercial acetate by precipitation with metallic lead, of copper, etc., conversion into sulphate, then into carbonate and reduction by potassic cyanide or black flux. (*Stas, Untersuch. über Chem. Prop. Leipzig*, 1867, 324.)

LITHIUM.

Regnault has determined the specific heat of lithium. It corresponds to an atomic weight of about 7. (*Gmelin-Kraut, l. c.*)

The earliest determinations of this constant seem to have been made with a double salt of lithium and potassium, at all events with a very impure material. According to Arfvedson, 420.4 lithium chloride give 1322.4 argentic chloride, whence he deduces as the atomic weight the number 127.757 [or 10.22.] (*Poggend. Ann.*, *8*, 1826, 189.) L. N. Vauquelin found 430 lithium sulphate equivalent to 875 barium sulphate. [If S = 32; Ba = 137.08, this relation gives Li = 9.27.] Vauquelin does not describe the preparation of his salt. (*Annal. de Chem. et de Phys.*, *7*, 1818, 287.) C. G. Gmelin found Li = 191.21 [or 7.65.] (*Poggend. Ann.*, *15*, 480; *Gilbert's Ann.*, *62*, 1819, 399.) Kralovanszky by two analyses of the sulphate with barium chloride got Li at from 10.096 to 10.168 (*Liebig's Ann.*, *121*, 94; *Schweigger's Journ.*, *54*, 1828, 231.) Thomson and Stromeyer also each got similar values. (*Thomson's System of Chem.*, 7th ed., *1*, 1831, 420.)

R. Hermann: *6.085* (O = 16); 38.03 (O = 100).

Experiments were made on the carbonate by decomposing it with acid over mercury, and measuring the resultant di-oxide. For C = 75.33, these determinations give Li = 38. Several experiments were also made by analyzing the sulphate with barium chloride. For S = 201.06 and Ba = 856.88, these give Li = 38.05. Hermann precipitated lithium carbonate with ammonium carbonate, and subsequently converted it into sulphate. The chloride was prepared from the phosphate by Berzelius' method. (*Poggend. Ann.*, *15*, 1829, 480.)

J. J. Berzelius: *6.533* (O = 16); 40.83 (O = 100).

Berzelius found that 1.874 lithium sulphate gave 3.9985 barium sulphate, and calculated this relation for S = 200.75; Ba = 855.29. He also found 4.4545 melted carbonate = 6.653 sulphate, but rejected the analysis. (*Lehrbuch*, *3*, 1229, and *Jahresbericht*, *10*, 1830, 96.)

R. Hagen: *6.57* (O = 16).

Hagen precipitated lithium sulphate with barium chloride, and found that 0.852 dry lithium sulphate gave 1.8195 barium sulphate whence he calculates Li = 6.493. [If Ba = 137.08; S = 32; this relation gives Li = 6.57.] (*Poggend. Ann.*, *48*, 1839, 363.)

J. W. Mallet: 6.95 (O = 16); 86.89 (O = 100).

In two experiments a known weight of lithium chloride was precipitated by argentic nitrate, and the argentic chloride weighed. In one experiment lithium chloride was titrated with argentic nitrate by Pelouze's method. The number is the mean; the extreme difference is 0.18 for O = 100. Mallet takes Ag = 1349.66; Cl = 443.28. The alkalis were separated from the lithium salt by repeated treatment with ether and alcohol. The salt was examined for impurities, and was fused with a little ammonium chloride to prevent the formation of oxy-chloride. (*Silliman's Amer. Journ.*, (2,) *22*, 1856, 349.)

L. Troost: 6.5 (O = 16).

Troost found this number from analysis of the carbonate which had been crystallized from water containing carbon di-oxide and dried at 200°, but does not regard it as definitive. (*Annal. de Chim. et de Phys.*, (3,) *51*, 1857, 111.)

J. W. Mallet: 7 (O = 16).

Troost having objected to Mallet's former method of determination, he redetermined it by precipitating the sulphate with a standard solution of barium chloride, the precipitating power of which had been tested on the sulphates of magnesium and sodium. This method was adopted to avoid the well-known imperfections of the sulphur determination. Compared with sodium sulphate the atomic weight of Li was found = 6.92 and 6.95. Compared with magnesium sulphate it was found = 7.07 and 7.09.

Mg = 24; Na = 23. The sulphate was prepared from carbonate, and dried somewhat below a red heat. (*Silliman's Amer. Journ.*, (2,) *28*, 1859, 349.)

K. Diehl: 7.026 (O = 16).

Determined by analysis of lithium carbonate with Bunsen's apparatus and in his laboratory. Four experiments; extreme difference, 0.024. C = 12. The salt was purified from alkalis by precipitation as carbonate, resolution in acid and reprecipitation, repeated until the sodium line was no longer visible. Diehl found that precipitation of the sulphate with barium chloride gave a nearly constant error on account of the retention of lithium in the precipitate, and led to nearly the same results as Berzelius got. (*Liebig's Ann.*, *121*, 1862, 93.)

L. Troost: 7 (O = 16).

Troost found 1.309 grammes lithium chloride = 4.42 argentic chloride, and 2.75 lithium chloride = 9.3 argentic chloride. From these analyses he deduces the values 7.03 and 6.99. By decomposing the carbonate, dried at 100°, with silicic acid, he found 0.97 carbonate = 0.577 carbon di-oxide and 1.782 carbonate = 1.059 di-oxide, and infers for Li 7 and 7.02. In one experiment the carbonate was converted into sulphate. 1.217 carbonate gave 1.808 sulphate. Troost calculates Li = 7.06. [If Cl = 35.457; Ag = 107.93; C = 12; S = 32; these determinations give, in the same order as above, 7.01; 6.94; 6.98; 7.02; 7.07.] The carbonate was purified by solution in water containing carbon di-oxide, and reprecipitation by boiling, the operation being repeated until the salt was spectroscopically pure. (*Paris Comptes Rend.*, *54*, 1862, 366.)

J. S. Stas: 7.022 (O = 16).

According to the mean of three determinations, 100 parts of silver = 39.358 lithium chloride; extreme difference, 0.005. If Ag = 107.93; Cl = 35.457; this ratio gives Li = 7.022. This value is confirmed by experiments on the conversion of the chloride into the nitrate, the results of which give Li = 7.018. The comparison with silver was made according to Pelouze's modification of the silver titration method. The chloride was purified from alkalis, after preliminary treatment with ether and alcohol, by pouring the dissolved salt into a boiling solution of ammonium car-

bonate containing ammonia in excess. All weighings reduced to vacuum. (*Stas, Untersuch. über Chem. Prop., Leipzig*, 1867.)

MAGNESIUM.

Regnault and Kopp have each determined the specific heat of this metal. It answers to an atomic weight of about 24. (*Gmelin-Kraut, l. c.*)

J. J. Berzelius: *25.3* (O = 16); 158.139 (O = 100).

Determined by dissolving magnesium oxide in dilute sulphuric acid, evaporating and heating to incipient redness. 100 oxide were found = 293.985 sulphate. The sulphate was perfectly soluble in water and had therefore lost none of its acid. The oxide was purified by solution in an aqueous solution of carbon di-oxide and reprecipitated by boiling. S = 200.75. (*Poggend. Ann.*, *8*, 1826, 188; and *Lehrbuch*, *3*, 1227.)

Marchand and Scheerer recalculated this analysis for S = 200 and reached the value 157.74. They assert that the oxide may have contained alkalis and that the sulphuric acid carries off magnesium sulphate in volatilizing. (*Erdmann's Journ. für Prak. Chem.*, *50*, 1850, 392.)

W. Henry: F. H. Wollaston: *23.36* (O = 16); 146 (O = 100).

Henry found that magnesium sulphate contained 33 per cent. magnesium oxide. If S = 200 the value follows. (*Phil. Trans.*, *104*, 1814, 21.)

— Longchamp: *15.35* (O = 16).

In two experiments, Longchamp found that five parts of crystallized magnesium sulphate are equivalent to 4.91 barium sulphate. [If Ba = 137.08; S = 32, the number follows.] Longchamp found 53 per cent. water which is much too high. According to Marchand and Scheerer, the data for the anhydrous salt give Mg = 97.37, for S = 200; Ba = 856.8, [or 15.74.] (*Annal. de Chim. et de Phys.*, *12*, 1819, 265.)

L. J. Gay-Lussac: *23.62* (O = 16).

16.205 grammes crystallized sulphate were found equal to 15.345 barium sulphate, and 19.395 magnesium sulphate

to 18.3455 barium sulphate. Calculating from the anhydrous salt Gay-Lussac found from these experiments respectively Mg =147.23 and Mg = 148.09 for Ba = 856.8; S = 200. The salt was found to contain 51.43 water. [Calculated from the anhydrous salt these data give Mg = 23.55 and 23.68. Calculated from the hydrous salt (7 molecules water) the numbers give 24.14 and 24.41, if S = 32; Ba = 137.08.] Gay-Lussac remarks that the sulphate is partially decomposed at a red heat. (*Annal. de Chim. et de Phys.*, *13*, 1820, 308.)

T. Scheerer: *24.16* (O = 16); 150.97 (O = 100).

Mean of six experiments on the precipitation of the sulphate with barium chloride. Extreme difference, 0.79. S = 200.75; Ba = 855.29. After weighing, the barium sulphate was treated with dilute HCl and the chloride thus extracted allowed for. (*Poggend. Ann.*, *69*, 1846, 535.)

T. Scheerer: *24.21* (O = 16); 151.33 (O = 100).

Barium sulphate formed as in the last determination was fused with soda, the barium carbonate dissolved in HCl, and reprecipitated as sulphate. In the filtrate additional magnesia was found. If the error in the former determination was the same, its corrected value would be as above. (*Poggend. Ann.*, *70*, 1847, 407.)

Svanberg and Nordenfeldt: *24.72* (O = 16); 154.504 (O = 100).

Four experiments were made on the calcination of the oxalate, and three on the conversion of the magnesia so obtained into sulphate. The oxalate was dried at from 100° to 105° and heated to redness until the weight was constant. The oxide was dissolved in sulphuric acid, evaporated and the excess driven off by heat. The oxalate was prepared from the sulphate by precipitation with sodium carbonate and digestion with oxalic acid. The number is the mean of all experiments; extreme difference, 0.514. S = 200.75; C = 75.12; H = 12.48. (*Erdmann's Journ. für Prak. Chem.*, *45*, 1848, 473.)

According to Marchand and Scheerer, the data give Mg = 154.27 for S = 200; H = 12.5; C = 75.

Marchand and Scheerer: *24.03* (O = 16); 150.19 (O = 100).

Eleven experiments were made in calcining massive magnesium carbonate from Frankenstein, and weighing the

caustic magnesia formed. The carbonate was dried at 300°, and the carbon di-oxide, which passes off above 230°, was caught by caustic baryta solution and determined. The traces of carbon di-oxide not expelled by a yellow heat were set free by solution in chlorhydric acid and also determined as barium carbonate. The silicic acid, etc., were also determined. The mean in air is 150.34; *in vacuo* as above. Extreme difference, 0.57. C = 75. Eleven other experiments were made with comparatively impure material and less precaution, tending to confirm the above. (*Erdmann's Journ. für Prak. Chem.*, *50*, 1850, 409.)

T. SCHEERER: 24 (O = 16); 150 (O = 100).

By separating the neutral sulphates of magnesium and calcium by means of alcohol, Scheerer found that the magnesites used by Marchand and himself contained from one-fourth to one-half per cent. calcium oxide. This correction would make their determination almost exactly 250 or 24. (*Liebig's Ann.*, *110*, 1858, 236.)

V. A. JACQUELIN: *24.408* (O = 16); 152.55 (O = 100).

Anhydrous, neutral magnesium sulphate, obtained by solution of the oxide in sulphuric acid and heating to redness, gave 33 56 per cent. pure oxide. The method adopted is not described. This oxide by treatment with sulphuric acid gave the original amount of sulphate. If S = 200, the number follows. (*Annal. de Chim. et de Phys.*, (3,) *32*, 1851, 195.)

A. MACDONNELL: 23.9 (O =16).

Determined from analyses of anhydrous and of crystaltized magnesium sulphate. (*Brit. Assoc. Rep.*, 1852, part 2, 36; and *Kopp's Jahresbericht*, *5*, 364.)

J. F. BAHR: *24.77* (O = 16); 154.842 (O = 100).

A known weight of purified magnesium oxide was dissolved in sulphuric acid, evaporated and heated to redness till the weight was constant. The number is the mean of three experiments; extreme difference, 0.515. The oxide was obtained from meteoric olivin. After removal of the heavy metals, the solution was evaporated to dryness with soda, washed and heated to redness. The oxide so obtained was dissolved in acetic acid, oxalic acid was added, the

solution evaporated nearly to dryness, and the oxalate thoroughly washed. Bahr says that the presence of alkalis could not be suspected. S = 200. (*Erdmann's Journ. für Prak. Chem.*, *56*, 1852, 310; *Œfversigt af Akad. Fœrh.*, 1851, 303.)

Scheerer says that oxide so prepared retains carbonic acid, that sulphate is carried off in heating the sulphate to redness, and that the presence of alkalis is to be suspected. (*Erdmann's Journ. für Prak. Chem.*, *56*, 1852, 489.)

J. Dumas: 24.6 (O = 16).

Dumas made eleven experiments on the titration of magnesium chloride with argentic nitrate. He found great difficulty in preparing pure chloride, and does not feel confident of his results. The number is the mean; extreme difference, 0.28. Ag = 108; Cl = 35.5. The chloride was prepared from various salts, but was in all cases finally heated in an atmosphere of HCl. Dumas points out, however, that this process does not remove oxide if present. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

MANGANESE.

Regnault has determined the specific heat of manganese. It corresponds to an atomic weight of about 55. (*Gmelin-kraut*, *l. c.*)

J. J. Berzelius: *56.93* (O = 16); 355.787 (O = 100).

By dissolving manganese in nitric acid, evaporating and heating to a low red, Berzelius found 100 Mn = 142.16 oxide. It was not known at the time that the oxide might be partially reduced by this process. (*Poggend. Ann.*, *8*, 1826, 185; and *Jahresbericht*, *9*, 136.)

J. A. Arfvedson: *56.25* (O = 16); 351.56 (O = 100).

From 1.508 chloride Arfvedson obtained 3.408 argentic chloride. If Ag = 1351.607; Cl = 221.325; the number follows. (*Berzelius' Jahresbericht*, *9*, 1829, 136; *Afhandl. i. Fysik.*, 6, 236.)

E. TURNER: *54.9* (O = 16).

Turner analyzed the carbonate in an apparatus similar to Bunsen's. He found 34.72 per cent. carbon di-oxide and 8.427 water. For C = 6, he calculates Mn = 28.024. By dissolving the protoxide in sulphuric acid, evaporating and heating to redness, he found 9 oxide = 19.01 sulphate. If S = 16, this gives Mn = 27.96. A second experiment gave 27.93. From 12.47 Mn chloride he obtained 28.42 argentic chloride. [If Cl = 35.5, Ag = 108; this gives Mn = 54.9.] The carbonate was obtained by precipitation with potassium carbonate. The protoxide was obtained by reduction of higher oxides in hydrogen. The chloride was melted in a current of HCl gas. (*Edinb. Trans.*, *11*, 1831, 143.)

J. J. BERZELIUS: *55.34* (O = 16); 345.9 (O = 100).

Berzelius repeated Turner's experiments, taking larger quantities. From the chloride he got from 345.84 to .96; from the sulphate from 346.03 to .29. Ag = 1351.607; Cl = 221.325; S = 201.165. (*Berzelius' Jahresbericht*, *9*, 1830, 136.)

J. J. BERZELIUS: *55.14* (O = 16); 344.684 (O = 100).

In his *Lehrbuch* he apparently takes the analyses of the chloride above cited, recalculated for Cl = 221.64; Ag = 1349.66. (*Lehrbuch*, *3*, 1224.)

R. BRANDES: *57.06* (O = 16); 356.602 (O = 100).

Determined by analysis of crystallized chloride. The chlorine was determined by precipitation with silver. The Mn was precipitated as carbonate, and converted into oxide by heat. The water was determined by difference, and the composition of the oxide was assumed to be as given by Berzelius, (!) whose values for Ag and Cl were also taken. (*Poggend. Ann.*, *22*, 1831, 256.)

K. VON HAUER: 54.98 (O = 16); 343.632 (O = 100).

Determined by nine experiments on the reduction of the sulphate to sulphide by heating the salt in a current of hydrogen sulphide. The reduction was performed in a porcelain tube enclosed in a charcoal fire. Number, mean; extreme difference, 0.34, for O = 16. The sulphate was prepared from a pyrolusite containing only silica, iron, and barium. It was reduced to protoxide, dissolved in sulphuric acid, oxidized with nitric acid, precipitated with oxalic

acid, converted into red oxide, dissolved in chlorhydric acid and alcohol, precipitated with ammonium carbonate, dissolved in sulphuric acid, repeatedly heated to redness and recrystallized, and was dried at 300°. Accurate experiments on the reduction of the red oxide proved impracticable on account of the hydroscopicity of the compound. Two experiments on the oxidation of the protoxide, undertaken as a check on the other method, gave 27.486 and 27.527 for O = 8; S = 16. (*Erdmann's Journ. für Prak. Chem.*, *72*, 1857, 361; *Sitz.-Bericht der k. k. Akad.*, 1857.)

J. DUMAS: 54.96 (O = 16).

Determined by the decomposition of the chloride with argentic nitrate. The number is the mean of five experiments; extreme difference, 0.1 for O = 16. Cl = 35.5; Ag = 108. Dumas had previously made experiments on the reduction of the hyperoxide to protoxide by hydrogen. These gave the atomic weight at from 25.99 to 26.09 for O = 8. Dumas believes that a part of the oxide was reduced to metal. The peroxide was prepared from nitrate of the protoxide. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 150.)

— RAWACK: 54.02 (O = 16).

Determined, in Schneider's laboratory, by reducing a known weight of red oxide to protoxide in a current of dry hydrogen, and weighing the water formed. The number is derived from the mean of six selected experiments. The extreme difference is 0.22 for O = 16. (*Poggend. Ann.*, *107*, 1859, 607.)

R. SCHNEIDER: 54.038 (O = 16).

The mean result of four analyses of the oxalate by the ordinary method of organic analysis. Extreme difference, 0.04 for O = 16. C = 12. The oxalate was prepared from chemically pure sulphate by precipitation with sodium carbonate, digestion with oxalic acid, and drying over sulphuric acid. (*Poggend. Ann.*, *107*, 1859, 613.)

MERCURY.

The specific heat of mercury in the solid state, as observed by Regnault, and the vapor density, as determined by Dumas, correspond to an atomic weight of slightly above 200. (*Gmelin-Kraut, l. c.; L. Meyer, l. c.*)

FOURCROY AND THENARD, DAVY, WOLLASTON: *200.8* (O = 16); 1255 (O = 100).

Fourcroy and Thenard found 8 O = 100 Hg. Davy found 30 O = 380 Hg, giving Hg = 1266. The latter also found 134 Cl = 380 Hg, which for Cl = 441, gives Hg = 1254. (*Phil. Trans.*, *104*, 1814, 21.)

N. G. SEFSTROEM: 202.53 (O = 16); 1265.822 (O = 100).

Determined by three analyses of the oxide according to which 100 Hg = 7.89, 7.9, and 7.97 O. (*Berzelius' Lehrbuch*, *3*, 1215.)

E. TURNER: *200.72* (O = 16).

Turner made a number of determinations of this atomic weight but regarded the value he adopted, 202, only as an approximation. From the oxide, prepared from nitrate, he got 200.77 and 199.97. The compound was decomposed by heat, and the products carried over silver and gold in a narrow tube. Four experiments were made on mercuric chloride which was decomposed by pure calcic oxide, and the Cl precipitated with argentic nitrate. [These analyses recalculated for the Stas' atomic weights of Ag and Cl give 202.079, 201.701, 201.815.] Turner also made two experiments on the reduction of the chloride with stannous chloride, the Hg being collected, dried and weighed. [These experiments recalculated give 199.423 and 199.289.] The mercuric chloride was purified by recrystallization. Weighings reduced to vacuum. (*Phil. Trans.*, *123*, 1833, 535.)

ERDMANN AND MARCHAND: *200.14* (O = 16); 1250.6 (O = 100).

Determined from the mean of four experiments on the reduction of the oxide in a current of carbon di-oxide. Copper, carbon (from sugar) oxide, and carbon, were introduced in successive layers in a combustion tube. Dry carbon di-oxide was passed through and the mercuric oxide heated. The metal was collected in a receiver to which a tube filled with gold foil was appended. The metal was perfectly clean. Moisture was removed by a stream of dry air after distillation. The oxide was purified by heating it to incipient decomposition the metallic fumes being removed

by a current of dry air. It was tested before being analysed. The extreme difference in the results was 0.8 for O = 100. All weighings *in vacuo*. (*Erdmann's Journ. für Prak. Chem.*, *31*, 1844, 392.)

E. MILLON: *199.94* (O = 16); 1249.63 (O = 100).

Millon made two experiments by heating mercuric chloride with calcic oxide in a current of hydrogen and condensing the metal. The experiments gave 73.87 and 73.82 per cent. mercury. If Cl = 442.64, the value follows. The chloride was dissolved in ether and sublimed. It was perfectly soluble in ether and alcohol, and was well crystallized. (*Paris Comptes Rend.*, *20*, 1845, 1291.)

L. SVANBERG: *200* (O = 16); 1250 (O = 100).

Svanberg made three experiments by the same method employed by Millon. The mean result was 1248.47; extreme difference, 0.94; but Svanberg shows that there was probably loss, and that the larger the quantity of chloride employed the higher the result. He regards Erdmann and Marchand's result as most probable, but in need of confirmation. Cl = 443.28. (*Erdmann's Journ. für Prak. Chem.*, *45*, 1843, 468; *Kongl. Vet. Akad. Handl.*, 1845, 135.)

MOLYBDENUM.

Regnault determined the specific heat of molybdenum. It answers to an atomic weight of about 96. (*Gmelin-Kraut*, *l. c.*)

J. J. BERZELIUS: *95.36* (O = 16); 596.1 (O = 100).

One hundred parts of anhydrous plumbic nitrate, dissolved and precipitated with neutral ammonium molybdate, gave 110.68 parts plumbic molybdate. If Pb = 1294.645, N = 87.53, the value follows. Berzelius expresses himself dissatisfied with the accuracy of the determination. (*Poggend. Ann.*, *8*, 1826, 23; and *Lehrbuch*, *3*, 1208.)

SVANBERG AND STRUVE: *92.13* (O = 16); 575.829 (O = 100).

After trying various methods without getting accordant results, these chemists made ten experiments on the sul-

phide by roasting it first in a current of moist, and then of dry air. Three experiments were excluded as imperfect. The remainder gave a mean of 89.7523 molybdic acid from 100 sulphide; extreme difference, 0.22. The value follows for S = 200. Objections have been made (*Liebig's Ann.*, *68*, 211) that the difference in weight between the acid and the sulphate is too small for the purpose of the determination, and that the different analyses give very different atomic weights. The sulphide was prepared by melting together molybdic acid, sulphur, and caustic potash, and leaching the product with water and chlorhydric acid. The sulphide was dried in a current of hydrogen. The molybdic acid was dissolved in ammonia to prove the absence of sulphide. (*Erdmann's Journ. für Prak. Chem.*, *44*, 1848, 315.)

N. J. Berlin: *91.96* (O = 16); 574.75 (O = 100).

Determined by four analyses of the double mono-sesqui-molybdate of ammonium by heating gently with nitric acid in a platinum crucible until only molybdic acid was left. Extreme difference, 3.32 for O = 100; N = 175; H = 12.5. The preparation of the salt is not given. (*Erdmann's Journ. für Prak. Chem.*, *49*, 1850, 446.)

J. Dumas: 96 (O = 16).

Dumas made five experiments on the reduction of molybdic acid (prepared from the natural sulphide) by means of hydrogen. The reduction was begun at a low temperature in a glass tube, and completed in an unglazed porcelain tube in a reverberatory furnace, where it was kept till several hours heating produced no further alteration in weight. The molybdenum did not assume a metallic appearance. The number is the mean; extreme difference, 0.8 for O = 16. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 142.)

M. Delafontaine: *92* (O = 16); 575 (O = 100).

This chemist made many experiments in various ways without being able to reach constant results, and only remarks that his experiments indicate Svanberg and Struve's value as the best. (*Erdmann's Journ. für Prak. Chem.*, *95*, 1865, 137; *Bibl. Univ., Arch. des Sciences*, *23*, 1865.)

H. Debray: 95.94 (O = 16).

Debray made three experiments on the reduction of molybdic acid. The acid was first converted into the red

oxide in platinum, and at a low temperature, and the small portion of the acid volatilized during this operation was caught and determined. The reduction was completed in a porcelain tube at a white heat. Debray gives his results at 48.03; 48.04; and 47.84. [The analytical data, recalculated, give 95.30; 95.55; 95.73; perhaps on account of misprints. Reduction to vacuum would still further reduce the numbers.] The acid was purified by sublimation in platinum, conversion into ammonium salt, and regeneration by heat. In two experiments ammoniacal solution of molybdic acid was evaporated in the dark with excess of argentic nitrate, the argentic molybdate dissolved out and the excess of silver determined. Debray found 5.510 acid = 7.657 silver, and 7.236 acid = 10.847 silver. Hence he calculates M = 48 and 47.98. [A little calculation shows that the first data are misprinted. They should read 5.11 acid = 7.657 silver. The corrected data give for Ag = 107.93; M = 96.06 and 95.99. The mean of the recalculated analyses is 95.73.] (*Paris Comptes Rend.*, *66*, 1868, 732.)

L. Meyer: *96.10* (O = 16).

Calculated from three analyses of the dichloride, two analyses of the tetrachloride, and two analyses of the pentachloride, made by Leichte and Kempe in Meyer's laboratory. The dichloride was analyzed by heating in a current of hydrogen sulphide, and subsequently in a current of hydrogen. Molybdenum disulphide is the residue. The HCl formed was caught in ammonium hydrate and precipitated by argentic nitrate, after the hydrogen sulphide had been driven off by boiling in a flask provided with a condensing drip-tube. The tetra and pentachloride were decomposed with nitric acid, excess of ammonium hydrate was added, and molybdenum trisulphide precipitated with ammonium sulphide. A weighed portion of the dry precipitate was converted into disulphide by heating in a current of hydrogen. The chlorine of the higher chlorides was determined in the filtrate after precipitation of the trisulphide. By comparing the amount of chloride analyzed with the amount of argentic chloride obtained, Meyer finds in mean M = 95.92; extreme difference, 1.87 for O = 15.96. By comparing the amount of disulphide with that of argentic chloride, M = 95.75; extreme difference, 1.35. By comparing the amount of chloride analyzed with the amount of disulphide obtained for one analysis of tetrachloride and two analyses of pentachloride, he gets M = 95.94; extreme difference, 2.15. The general mean is M = 95.86; extreme

difference, 2.15. Ag = 107.66; S = 31.98; Cl = 35.37; O = 15.96. The specific gravities of the chlorides not having been determined, the weighings are not reduced to vacuum. The pentachloride was prepared from M by heating it in a current of Cl entirely free from air. The metal had been freed from oxide by heating in an atmosphere of HCl. By moderate heating of the pentachloride in dry H, and by distilling pentachloride over the product in dry carbon di-oxide, the trichloride is obtained. The trichloride heated in carbon di-oxide is decomposed into tetrachloride and di-chloride, which latter must be purified with warm dilute nitric acid. (*Liebig's Ann.*, *169*, 1874, 360, 344.)

NICKEL.

Regnault has determined the specific heat of nickel. It corresponds to an atomic weight of about 59. (*Gmelin-Kraut, l. c.*)

E. Rothoff: *59.09* (O = 16); 369.333 (O = 100).

Rothoff converted 188 parts of oxide into chloride, a neutral solution of which gave 718.2 parts argentic chloride. If Cl = 221.64, Ag = 1349.66, the value follows. (*Berzelius' Lehrbuch*, *3*, 1221.)

P. Berthier.

Lassaigne having announced the atomic weight of nickel at 500, (*Schweigger's Jahrbuch*, *9*, 108,) Berthier re-examined the subject and found Rothoff's number confirmed. (*Berzelius' Jahresbericht*, *5*, 1825, 148; *Annal. de Chim. et de Phys.*, *25*, 1824, 148.)

Erdmann and Marchand: *58.2* (O = 16); 365.9 (O = 100).

Determined "with all precaution" by the reduction of the oxide with hydrogen. The results varied from 29.1 to 29.3, but Erdmann has reason to believe the smaller number the more accurate. (*Erdmann's Journ. für Prak. Chem.*, *55*, 1852, 202.)

H. Sainte-Claire Deville:

100 parts fused nickel, containing three-tenths per cent. silicon and one-tenth per cent. copper, gave 262 parts anhydrous, yellow nickel sulphate, "corresponding to the atomic weight as given by Berzelius." (*Annal. de Chim. et de Phys.*, (3,) *46*, 1856, 182.)

R. Schneider: 58.05 (O = 16); 362.8 (O = 100).

Determined from four analyses of the oxalate. The carbon determinations were made by the ordinary method of organic analysis, because some hydrocarbon forms when the salt is decomposed by heat alone. The metal was determined by heating a known weight of the salt first in air and then in a current of oxygen, and subsequent reduction by hydrogen. In the preparation of the salt the usual precipitate with ammonium sulphide was washed with dilute chlorhydric acid, and the cobalt separated with barium carbonate and chlorine. From the nickel salt obtained the oxalate was precipitated with oxalic acid. The number is the mean of four analyses; extreme difference, 0.082 for O = 8. (*Poggend. Ann. 101*, 1857, 396.)

C. Marignac: 59 (O = 16).

Marignac made two analyses of the sulphate by decomposing the salt by heat. The decomposition is perfect. To avoid errors arising from possible reduction of a portion of the oxide, it was moistened with nitric acid, and recalcined at a moderate temperature. The results obtained were Ni = 29.2 and 29.5. The sulphate was purified by recrystallization. He also made experiments on the chloride by titration with argentic nitrate, according to Pelouze's modification of Gay-Lussac's method. Three such analyses gave from 29.4 to 29.5. In one experiment he also evaporated the nickel nitrate, after filtering off the argentic chloride, and converted it into oxide by heat. This experiment gave Ni = 29.64. The chloride, whether it be distilled or calcined with ammonium chloride, is apt to leave an insoluble residue the weight of which must be deducted. S = 16; Ag = 108; Cl = 35.5. (*Bibl. Univ. Arch. des Sciences*, (2,) *1*, 1858, 375.)

J. Dumas: 59.028 (O = 16).

The number is the mean result of five experiments on the titration of the chloride with argentic nitrate; ex-

treme difference 0.08. Ag = 108; Cl = 35.5. In three cases the nickel chloride was prepared by dissolving fused nickel in aquia regia, repeated evaporation to dryness with HCl, and heating for from twelve to twenty-four hours in a current of HCl gas. In two cases it was produced by passing a current of chlorine over spongy nickel. The chloride analyzed was crystalline and volatile without residue. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 149.)

R. Schneider: 58.058 (O = 16).

In consequence of Marignac's criticism (that as nickel oxalate is insoluble it cannot be purified by recrystallization) Schneider repeated his former determination, making special tests for oxalic acid, sodium, and chlorine, with the above result. (*Poggend. Ann.*, *107*, 1859, 616.)

W. J. Russell: 58.738 (O = 16).

Determined from the mean of thirteen experiments on the reduction of the oxide in hydrogen. Extreme difference, 0.12 for O = 16. The oxide was prepared from three specimens of commercial nickel, which were first converted into pure oxalate and then into nitrate. The oxide was obtained by decomposing the nitrate by a very strong heat. (*Journ. Chem. Soc.*, (2,) *1*, 1863, 61.)

Schneider remarks that a portion of the oxide analyzed may have been reduced during the process of decomposing the nitrate. (*Poggend. Ann.*, *130*, 1867, 310.) Marignac points out the same danger. (*Bibl. Univ., Arch. des Sciences*, (2,) *1*, 374.)

E. von Sommaruga: 58.026 (O =16).

Determined from the amount of barium sulphate obtained by precipitating the double sulphate of nickel and potassium with barium chloride. The number is the mean of six experiments; extreme difference, 0.168 for O = 8, S = 16; Ba [no doubt] = 68.5; K = 39.2. The salt was prepared by solution of commercial nickel in sulphuric and nitric acid, adding potassic sulphate to the solution, and repeatedly recrystallizing the double sulphate. (*Erdmann's Journ. für Prak. Chem.*, *100*, 1867, 115; *Sitz.-Ber. der k. k. Akad.*, 1866.)

C. Winkler: 59.05 (O = 16).

Determined by the amount of gold precipitated from a solution of neutral crystallized potassium chloro-aurate by

a known weight of nickel. The number is the mean of four experiments; extreme difference, 0.186 for O = 16, Au = 196. The nickel was prepared as follows: commercial nickel carbonate was dissolved in chlorhydric acid, cobalt was repeatedly precipitated with sodium hypochlorite, copper, etc., were removed with hydrogen sulphide, the nickel was precipitated with sodium carbonate, the precipitate dissolved in chlorhydric acid, the chloride sublimed and reduced in a current of hydrogen. (*Fresenius' Zeitsch.*, *6*, 1867, 22.)

W. J. Russell: 58.76 (O = 16).

Determined by the amount of hydrogen set free by solution of nickel in chlorhydric acid. The nickel was that obtained in Russell's former determination of the atomic weight of nickel. (*Chem. News*, *20*, 1869, 20.)

R. H. Lee: 58.01 (O = 16).

Determined by analyses of nickel cyanide salts. They were decomposed in a platinum crucible by heat from above. The carbon separated out was burned off first in air and then in oxygen. The metallic oxide was reduced in a current of hydrogen. The mean of six experiments on the strychnine salt gave Ni = 58.04. The mean of six experiments on the brucine salt gave Ni = 57.98. The salts were purified by recrystallization. (*Berlin. Bericht der Chem. Ges.*, *4*, 1871, 790.)

NIOBIUM.

The vapor density of the chloride and of the oxychloride, as determined by Deville and Troost, places the atomic weight at about 94. (*Paris Comptes Rend.*, *56*, 1863, 891.)

H. Rose: *122* (O = 16).

Rose deduced the atomic weight of niobium from analyses of what he supposed to be the tetrachloride, determining the niobium as niobic acid, and the chlorine as argentic chloride. The results, which varied greatly, indicated the value 97.64. [Marignac having proved that the salt is a pentachloride, this number becomes 122.] Marignac showed

that Rose dealt with a compound containing a large amount of the corresponding tantalium chloride. (*Poggend. Ann.*, *104*, 1858, 439.)

ROSE; RAMMELSBERG: 94 (O = 16).

Rose analysed the oxychloride, but did not recognize it as an oxychloride. Rammelsberg calculated the atomic weight from Rose's figures and found that the highest chlorine contents corresponds to an atomic weight of 94. Rose's salt must have been nearly pure as there is no corresponding tantalium compound. (*Poggend. Ann.*, *136*, 1869, 353.)

R. HERMANN: 104.8 (O = 16).

Hermann deduces this value from analyses of a number of chlorides and sodium salts. The formulas which he gives these compounds are complicated, unlikely, and unsupported by evidence. Marignac has shown that Hermann's salts contained tantalium. (*Erdmann's Journ. für Prak. Chem.*, *68*, 1856, 73.)

C. W. BLOMSTRAND: 95 (O = 16).

Blomstrand made three determinations of the chlorine contents of the pentachloride, getting 64.712 per cent., extreme difference, 0.32. He also made eleven determinations of the niobium in the same compound, weighing it as niobic acid. 100 chloride gave in mean 49.794 acid. The atomic weight calculated from the chlorine contents is 96.67; from the niobic acid, 96.16. Blomstrand also made experiments on sodium niobate which led him to the conclusion that the most probable number is 95. (*Gmelin-Kraut*, *2*, part 2, 73; *Acta Univ. Lund.*, 1864.)

C. MARIGNAC: 94 (O = 16).

Determined from a number of analyses of potassium fluoniobate containing two atoms of potassium. The compound was decomposed by sulphuric acid with which it was evaporated to dryness. The residue was leached with water, the filtrate evaporated and the potassic sulphate melted and weighed. The sulphuric acid remaining with the niobic acid was driven off by heat and the acid weighed. The salt being readily soluble and crystallizing well, can easily be purified from all substances except titanium which Marignac knows no way of separating or determining.

The larger the amount of titanium present, the lower will the atomic weight be; Marignac therefore takes the highest value. (*Liebig's Ann., S.* 4, 334, 288, 338; *Bibl. Univ., Arch. des Sciences, 23*, 1865, *25*, 1866.)

NITROGEN.

Regnault has determined the specific gravity of nitrogen. It indicates an atomic weight slightly above 14. (*Gmelin-Kraut, l. c.*)

BIOT and ARAGO; WOLLASTON: *14.03* (O = 16); 87.7 (O = 100).

Biot and Arago found the specific gravities of N and H 0.96913 and 0.07321. If H = 13.27 the value follows. [This very accurate value is of course the result of two compensating errors.] (*Phil. Trans., 104*, 1814, 20.)

J. J. BERZELIUS; *14.163* (O = 16); 88.518 (O =100).

Calculated from the specific gravity as determined by Berzelius and Dulong, compared with that of oxygen. By decomposing the nitrate of lead by heat, Berzelius also found N = 88.61 for Pb = 1294.498. (*Poggend. Ann., 8*, 1826, 14.)

E. TURNER: 14.15 (O = 16).

Determined by experiments on the nitrates of lead, silver, and barium, which were precipitated with sulphuric and hydrochloric acids, and gave respectively N = 14.201; 14.09; 14.17; if Pb = 103.6; Ba = 68.7; Cl = 35.42; S = 16.085; the weighings being reduced to vacuum. The salts were purified by recrystallization. Turner recommends more direct methods. (*Phil. Trans., 123*, 1833, 537.)

T. THOMSON: *14* (O = 16).

From the hypothesis that air is a compound containing four parts of N and one part oxygen, and from the average of various selected determinations of the specific gravity of oxygen, Thomson concludes the specific gravity of oxygen is 1.1111, and that of N 0.9722. These numbers stand

to one another as 16 to 14. (*Erdmann's Journ. für Prak. Chem.*, *8*, 1836, 375; *Records of General Science, by R. D. Thomson*, 1836, 179.)

F. Penny: 14.018 (O = 16).

From the mean of three series of experiments (vide Penny's determination of potassium) it follows that 100 potassic chloride = 135.636 potassic nitrate. Penny found the molecular weight of KCl = 74.527; hence the difference between a chloride and a nitrate is 26.560. Similar experiments were made on the sodium salts. In four experiments 100 sodium chlorate were found = 54.930 chloride; extreme difference, 0.02. In three experiments, 100 sodium chlorate were found = 79.882 sodium nitrate; extreme difference, 0.015. In six experiments 100 sodium nitrate were found = 68.771 chloride; extreme difference, 0.013. In seven experiments 100 chloride were found = 145.416 sodium nitrate; extreme difference, 0.016. These data give sodium chloride = 58.5, and the nitrate = 85.068, or the difference between a chloride and a nitrate = 26.568. Penny found Cl = 35.454. If $NO_3 - Cl = 26.564$, N = 14.018. Weighings for vacuum. (*Phil. Trans.*, *129*, 1839, 25.)

L. Svanberg: *13.91* (O = 16).

Determined by four experiments on the decomposition of plumbic nitrate by heat which gave a mean of 67.4016 per cent. oxide; extreme difference, 0.0087. [If Pb = 206.926 (Stas) the value follows.] (*Berzelius' Jahresbericht*, *22*, 1842, 38.)

C. Marignac: *14.02* (O = 16); 87.625 (O = 100).

Marignac made five experiments by dissolving a known weight of silver in nitric acid and melting and weighing the nitrate formed. The silver carried out of the retort by the vapors was precipitated and determined. The mean result was that 100 silver = 157.430 nitrate; extreme difference, 0.046; or, if Ag = 1349.01, N = 87.535. Six experiments were made by the decomposition of a known weight of argentic nitrate with a known weight of potassic chloride by Pelouze's method. Mean, 100 KCl = 227.986 argentic nitrate; extreme difference, 0.18. This gives N = 87.685 if K = 488.94 and Cl = 443.2. Seven experiments by the same method showed that 100 silver dissolved in nitric acid = 49.522 ammonium chloride; extreme differ-

ence, 0.063; Hence N = 87.655. The weighings are reduced to vacuum. (*Berzelius' Jahresbericht*, *24*, 1842, 44; *Bibl. Univ. de Genève*, *46*, 1842, 363.)

T. ANDERSON: *13.95* (O = 16); 87.204 (O = 100).

Determined by four experiments on the decomposition of plumbic nitrate by heat at a sufficiently low temperature to permit of complete decomposition. The number is the mean; extreme difference, 0.198 for O = 100. Pb = 1294.5. (*Annal. de Chim. et de Phys.*, (3,) *9*, 1843, 254.)

J. PELOUZE: *14.014* (O = 16); 87.59 (O = 100).

A known weight of argentic nitrate was brought in contact with a known and slightly excessive weight of ammonium chloride and the excess titrated with silver solution. One experiment gave N = 175.58; a second gave N = 174.78. Ag = 1349.01; Cl = 443.2. The ammonium chloride was purified by sublimation and recrystallization. (*Paris Comptes Rend.*, *20*, 1845, 1047.)

P. EINBRODT: *14* (O = 16); 87.5 (O = 100).

Experiments on the decomposition of plumbic nitrate by heat gave N = 87.5 plus a vanishing quantity if Pb = 1294.2239. (*Leibig's Ann.*, *70*, 1849, 286.)

J. DUMAS: 14 (O = 16).

Determined by experiments on the combustion of ammonia and cyanogen. Particulars not given. C = 6; H = 1. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 134.)

J. S. STAS: 14.044 (O = 16).

Stas made seven determinations of the relation between silver and its nitrate by dissolving pure silver in nitric acid, evaporating to dryness and keeping the salt melted until there was no further loss of weight. In two of these experiments the salt was melted *in vacuo*. The mean result was that 100 Ag = 157.472 nitrate; whence N = *14.040*. Later Stas made two more experiments by the same method with all possible precautions to secure accuracy. These gave 100 Ag = 157.484 nitrate and N = 14.042. By the conversion of the chlorides of potassium, sodium, lithium and silver into nitrates, Stas found the difference between a chloride and a nitrate 26.5882. This gives N = 14.045. The weigh-

ings are reduced to vacuum. Cl = 35.457; Ag = 107.93. (*Stas, Unters. über Chem. Prop. Leipzig*, 1867.)

OSMIUM.

Regnault has determined the specific heat of osmium. It corresponds to an atomic weight of about 199. (*Gmelin-Kraut, l. c.*)

J. J. Berzelius: *199.04* (O = 16).

Berzelius analyzed potassium chloro-osmate by reduction in a current of hydrogen and solution of the potassium chloride from the residue. 1.3165 grammes of the double salt lost 0.3805 in reduction and the residue was composed of 0.401 potassium chloride and 0.535 osmium. The atomic weight may be calculated either from the chlorine lost or from the relation of the chloride to the metal in the residue. Berzelius preferred the latter as more probably accurate. [If K = 39.137; Cl = 35.457 (Stas;) this relation gives 199.04.] According to W. M. Watts, (Chem. News, *19*, 302) the loss of chlorine gives for Stas's values Os = 199.42. Hyperosmic acid was separated from iridium compounds by distilling at a gentle heat. The first portion is perfectly pure. The metal was precipitated from chlorhydric acid solution of hyperosmic acid by mercury and subsequently purified by heating in a current of hydrogen. Potassium chloro-osmate was formed by heating comminuted metal and KCl in a current of chlorine. (*Poggend. Ann.*, *13*, 1828, 530; *Kongl. Vet. Acad. Handl.*, 1828.)

E. Fremy: *199.65* (O = 16); 1247.8 (O = 100).

Pure osmium was burned in a current of oxygen and the fumes led over potassic hydrate, by which they are absorbed. An additional potash tube did not increase in weight. Corks were avoided. Number of experiments not given. (*Erdmann's Journ. für Prak. Chem.*, *33*, 1844, 409; *Journ. de Pharm. et Chim.*, 1844, 241.)

Deville and Debray: 198 (O = 16).

These chemists determined the vapor density of hyperosmic acid by Dumas' method, finding it 8.89 at 246°,

and 8.87 at 286°. They hence consider it probable that the atomic weight of osmium is the same as that of platinum. The acid was very pure and was prepared by the combustion of metallic osmium in oxygen. (*Paris, Comptes Rend.*, *44*, 1857, 1101.)

OXYGEN.

The atomic weight of oxygen is assumed at 16 for the reasons stated under hydrogen, q. v. If hydrogen is taken as unity, O = 15.96.

PALLADIUM.

Regnault determined the specific heat of palladium. It corresponds to an atomic weight of about 106. (*Gmelin-Kraut, l. c.*)

J. J. Berzelius; *106.51* (O = 16).

In his earliest determinations of this constant, Berzelius saturated the metal with sulphur, getting about 711 for S = 201.165; and decomposed the chloride with mercury, getting 704. [711 appears to be a misprint for 714.618 the number given with corresponding data at Poggend., *8*, 180.] In this investigation a known weight of potassium chloropalladate was reduced in a current of hydrogen, the weight of the residue determined, the potassium chloride leached from the residue and the metallic palladium weighed. The double salt was strongly heated, but not to fusion, in a current of dry air before weighing. It being impossible to desiccate this and the similar platinum-metal salts completely without decomposition, the atomic weight was calculated from the relation between the metal and the KCl. Berzelius found 0.575 Pd = 0.809 KCl, and 0.851 Pd = 1.192 KCl. [If KCl = 74.594 (Stas) the former gives Pd = 106.036, the latter 106.509.] Berzelius had reason to consider the latter analysis the more accurate. (*Poggend. Ann.*, *13*, 1828, 454; *Kongl. Vet. Acad. Handl.*, 1828.)

PHOSPHORUS.

The specific heat of this element, as well as the density of phosphorus and its numerous volatile compounds in the gaseous state, corresponds to an atomic weight slightly above 31. (*Gmelin-Kraut, l. c.*)

V. ROSE; F. H. WOLLASTON: *35.1* (O = 16).

Wollaston adopted the analysis of Rose, who found that phosphoric anhydride contained 53.28 per cent. oxygen and 46.72 per cent. phosphorus. [This relation gives the above value.] (*Phil. Trans.*, *104*, 1814, 20.)

J. J. BERZELIUS: *31.325* (O = 16).

Berzelius made experiments on the reduction of auric chloride and of argentic sulphate by phosphorus. His results were 0.8115 P = 13.98 Ag; 0.829 P = 8.714 Au; 0.754 P = 7.93 Au. [The first of these analyses is misprinted in the original memoir (Gilbert's Ann., *53*, 433).] In the *Lehrbuch* it is miscalculated as Ruecker has shown. Berzelius preferred deducing the atomic weight of P from that of silver, because the atomic weight of the latter was more accurately known than that of gold. [If Ag = 107.93, the data give P = 31.325, for Au = 196.67 the latter analyses give P = 31.176 and 31.165.] In all the experiments the precipitated metal was boiled with the solution when the reduction was nearly complete. A trace of gold was observed to precipitate after the experiments were over. The silver was heated to redness before weighing. [J. P. Cooke, Jr., has shown (atomic weight of antimony) that silver is volatile at a red heat. Berzelius must therefore have got too large a result.] The phosphorus was distilled, melted in a glass tube and cooled very slowly, to permit traces of oxides to rise to the surface, and the lower portion of the tube with the phosphorus broken off and instantly weighed. (*Gilbert's Ann.*, *53*, 1816, 433, and *Lehrbuch 3*, 1188.)

J. PELOUZE: *32.024* (O = 16); 200.15 (O = 100).

A known weight of argentic nitrate was brought in contact with a known and slightly excessive weight of phosphorous chloride and the excess titrated. The number of experiments is not given. Ag = 1349.01; Cl = 443.2.

The terchloride was prepared by chloridizing finely divided P with dry chlorine, adding finely divided P, decanting, agitation with tin amalgam and rectification over the same. The fluid was colorless and did not give any precipitate with water. (*Paris, Comptes Rend.*, *20*, 1845, 1047.)

V. A. Jacquelin: *29.83* (O = 16); 186.438 (O = 100).

Determined by experiments on the chlorides of phosphorus with argentic nitrate and plumbic oxide. The results are utterly discordant. (*Paris, Comptes Rend.*, *33*, 1851, 693.)

A. Schroetter: 31.0274 (O = 16).

Determined by burning perfectly pure amorphous phosphorus in dry oxygen and weighing the phosphoric anhydride. The number is the mean of 10 experiments; extreme difference, 0.1242. Previous to burning, the phosphorus was heated for a long time in carbon di-oxide or hydrogen. It was burned not in powder but in lumps. (*Erdmann's Journ. für Prak. Chem.*, *53*, 1851, 435; *Sitz.-Bericht der k. k. Akad.*, 1851.)

B. C. Brodie: 31.31 (O = 16).

Three experiments made by oxidation of phosphorus with aqua regia and determination as magnesium pyrophosphate gave this mean. Brodie seems to regard these determinations only as evidence that the atomic weight needs redetermination. (*Journ. Chem. Soc.*, *5*, 1852, 295.)

J. Dumas: 31.03 (O = 16).

Determined by five experiments on the titration of the terchloride with argentic nitrate. The chloride was prepared by the action of dry chlorine on amorphous phosphorus and distillation after the chlorine had been displaced by carbon di-oxide. The portion distilling between 76° and 78° only was used. The number is the mean of the results; extreme difference, 0.08. Ag = 108; Cl = 35.5. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 172.)

PLATINUM.

Regnault and Kopp have determined the specific heat of platinum. It answers to an atomic weight of about 197. (*Gmelin-Kraut, l. c.*)

J. J. Berzelius: *197.19* (O = 16).

Determined by the same method as osmium, q. v., from a single experiment on potassium auroplatinate. 2.135 potassium chloride accompanied 2.822 platinum. [If KCl = 74.594 (Stas,) this gives the above value.] The salt was prepared by precipitating an alcoholic solution of platinum chloride with potassium chloride, washing with alcohol and heating to redness in a current of chlorine. Berzelius remarks that the metal used in his former determinations was impure. (*Poggend. Ann.*, *13*, 1828, 468, and *Lehrbuch*, *3*, 1213.)

T. Andrews: 197.88 (O = 16).

Determined by three experiments on potassium chloroplatinate. The salt was dried at 105° in vacuo, decomposed by zinc, the excess of zinc removed by acetic acid, the solution filtered off, and the chlorine titrated. The number is the mean; extreme difference, 0.22. The values assumed for Ag and Cl are not given. They were most likely Marignac's. (*Brit. Assoc. Rep.*, 1852, part 2, 33.)

J. S. Stas made preparations for determining the atomic weight of platinum, but not being able to produce potassium chloroplatinate entirely free from water, and being unacquainted with Bunsen's method of accomplishing this end, resigned the attempt. He made, indeed, three analyses by the same method employed by Berzelius, but unfortunately does not communicate the results. (*Stas*, *Untersuch. über Chem. Prop.*, *Leipzig*, 1867, 265.)

POTASSIUM.

Regnault determined the specific heat of potassium. It corresponds to an atomic weight of about 39. (*Gmelin-Kraut, l. c.*)

M. H. Klaproth ; F. H. Wollaston : *39.517* (O = 16).

Klaproth found that 441 Cl = 591 potassium oxide. Hence Wollaston deduced the value 491 (O = 100) for K. [If Cl = 35.457, this relation gives K = 39.517.] (*Phil. Trans.*, *104*, 1814, 20.)

J. J. Berzelius : *39.193* (O = 16) ; 244.958 (O = 100).

Berzelius found that 100 KCl = 192.4 Ag Cl. If Ag = 1351.607 ; Cl = 442.65 ; the above value follows. (*Poggend. Ann.*, *8*, 1826, 190.)

F. Penny : 39.073 (O = 16).

Penny made six experiments on the conversion of the chlorate into the chloride. Potassic chlorate was dried at about 105°, dissolved in a flask with HCl, evaporated, dried and weighed. The cake contained some free HCl. It was broken up, pulverized, and a known quantity heated to dull redness but not to fusion, and the HCl expelled allowed for. The mean result was that 100 $KCl\ O_3$ = 60.823 KCl ; extreme difference, 0.015. This relation gives KCl = 74.527 and if Cl = 35.454 (Penny,) the value for K follows. Numerous experiments were also made on the introconversion of the nitrate, the chloride and the chlorate, which established the difference between a chloride and a nitrate, besides confirming the value of K. The salts were purified by recrystallization and were carefully tested for impurities. The weighings are all for vacuum. (*Phil. Trans.*, *129*, 1839, 18.)

C. Marignac : *39.2* (O = 16); 245 (O = 100).

By six experiments on the decomposition of the chlorate by heat, 100 chlorate were found to lose 39.161 oxygen ; extreme difference 0.012 ; hence KCl = 932.14. By comparing this value with the molecular weight and the composition of argentic chloride, Cl was calculated at 442.13, leaving for K the number 490. Confirmatory experiments were made on potassic perchloride. The chlorate was purified by recrystallization. The weighings are for vacuum. (*Liebig's Ann.*, *44*, 1842, 23.)

C. MARIGNAC: *39.115* (O = 16); 244.47 (O = 100).

Having determined the atomic weight of chlorine from syntheses of argentic chloride, and found it 443.2, the molecular weight of KCl in the last determination, gives K = 244.47, for vacuum. Berzelius, by rejecting some analyses and the correction for vacuum, deduces the value 244.429. (*Berzelius' Jahresbericht*, *25*, 1845, 31; *Bibl. Univ. de Genève*, *46*, 1842, 350.)

J. PELOUZE: *39.144* (O = 16); 244.65 (O = 100).

A known weight of KCl was brought into contact with a known amount of silver dissolved in nitric acid, the chloride being slightly in excess. This excess was titrated with a decimal solution of silver. The number is the mean of three experiments. Ag = 1349.01; Cl = 443.2. The chloride was prepared by heating the chlorate and recrystallizing the residue. (*Paris Comptes Rend.*, *20*, 1845, 1047.)

According to Pelouze, Levol found the molecular weight of KCl 466.245, which combined with Marignac's value of Cl would give K = 244.645 or *39.143*. (*Ibid.*)

E. J. MAUMENÉ: *38.96* (O = 16); 243.502 (O = 100.)

The mean of three experiments on the decomposition of KCl with an excess of argentic nitrate showed that 100 KCl = 192.75 AgCl. If Ag = 1350.32 and Cl = 443.67, according to Maumené's determinations, the number follows. The KCl was prepared from the chlorate by heat. To confirm his values for K and Cl, he made seven experiments on the decomposition of the chlorate by heat, and found that 100 chlorate gave 60.791 chloride. An unaccounted for increase in the weight of the flask occurred in these experiments. (*Annal. de Chim. et de Phys.*, (3,) *18*, 1846, 41.)

J. S. STAS: 39.137 (O = 16).

According to the mean of seven determinations, 100 parts of KCl dissolved in nitric acid, and evaporated to dryness give 135.6423 parts of nitrate; extreme difference, 0.017. If Cl = 35.457; N = 14.044; the value follows. This value is confirmed by previous experiments which gave 39.130. Potassic chloride, by whatever means it is prepared, still retains silica. Stas, therefore, determined

the amount of silica in the KCl and allowed for it. Weighings for vacuum. (*Stas, Untersuch. über Chem. Prop., Leipzig*, 1867.)

Stas mentions that Dumas, who was the first to place K at 39, afterwards became convinced that this number was too low. (*Ibid*, page 318.)

RHODIUM.

Regnault has determined the specific heat of rhodium. It corresponds to an atomic weight of about 104. (*Gmelin-Kraut, l. c.*)

J. J. Berzelius : *104.3* (O =16).

Berzelius made two analyses of dipotassic chlororhodiate. This salt can be completely desiccated in a current of chlorine at a red heat without decomposition. 3.146 grammes gave on reduction in a current of hydrogen 0.930 Cl, and the residue contained 1.304 KCl and 0.912 metallic rhodium. [If KCl = 74.594, Cl = 35.457, (Stas,) the atomic weight of the salt calculated from the Cl contents is 359.831, and that of Rh 104.272. The relation between the Rh and the Cl gives Rh =104.312. The relation between the KCl and the Rh gives Rh = 104.340. The mean is 104.308.] Berzelius made a second analysis of the crystallized salt in which he determined the water of crystallization. [Under the same suppositions and in the same order, the resulting values for Rh are 106.279; 104.762; 103.708.] In the *Lehrbuch* only the former analysis is used to deduce the atomic weight. Rhodium was separated from other metals by its insolubility in aqua regia. The double salt was formed by heating finely pulverized Rh in mixture with KCl in a current of chlorine. The double salt was dissolved in water, precipitated with alcohol, washed with alcohol and dried. (*Poggend Ann.*, *13*, 1828, 437; *Kongl. Vetens. Akad. Handl.*, 1828.)

In his earlier determination (Rh = 750.68 for O = 100) Berzelius mistook an hydrated oxide for a chloride. (*Ibid.*)

RUBIDIUM.

Kopp determined the specific heat of rubidium chloride. It corresponds to an atomic weight of about 85. (*Gmelin-Kraut, l. c.*)

KIRCHHOFF and BUNSEN: 85.36 (O = 16).

Determined from the mean of four experiments on the precipitation of the chloride with argentic nitrate. The extreme difference was 0.24. Ag = 107.94; Cl = 35.46. An impure mixture of rubidium and potassium chlorides, nearly free from lithium and the earths, was partially precipitated with platinum chloride and the precipitate freed from KCl by repeated boiling with water. The residue was reduced in a current of hydrogen, the rubidium chloride extracted with water, and reprecipitated with platinum chloride. This process was repeated until the potassium lines in the spectrum disappeared. The rubidium was then converted into a mixture of carbonate and oxide, and the caesium separated by extraction with alcohol. The amount of silver precipitated was also tested from time to time and the purification continued till this became constant. (*Poggend. Ann.*, *113*, 1861, 339.)

J. PICCARD: 85.41 (O = 16).

Determined by four analyses of rubidium chloride with argentic nitrate. The number is the mean; extreme difference, 0.09. The separation of potassium from rubidium was effected for the different analyses by 6, 7, and 8 successive partial precipitations with platinum chloride, and the separation of caesium by thirty successive extractions of the anhydrous carbonates with warm absolute alcohol. The salt analysed was spectroscopically pure. Ag = 107.94; Cl = 35.46. The experiments were made with Bunsen's assistance. (*Erdmann's Journ. für Prak. Chem.*, *86*, 1862, 449.)

L. Grandeau, who is sometimes credited with making a determination of Rb, expressly disclaims doing so. He mentions Bunsen's value as the true atomic weight and says that his analyses of the sulphate, undertaken to test its purity, led him to adopt the number 85.4; apparently for brevity's sake. (*Annal. de Chim. et de Phys.*, (3,) *67*, 1863, 227.)

R. Godeffroy: 85.476 (O = 16).

Determined by four analyses of rubidium chloride prepared and analysed exactly as Godeffroy determined cæsium, q. v.; extreme difference, 0.04. Cl = 35.5; Ag = 108. (*Liebig's Ann.*, *181*, 1877, 189.)

RUTHENIUM.

Bunsen has determined the specific heat of ruthenium. It corresponds to an atomic weight of about 104. (*Gmelin-Kraut*, *l. c.*)

C. E. Claus: *104.57* (O = 16).

Determined from three analyses of potassium chlororutheniate by the same method Berzelius had employed for other platinum metals. Claus found an average of 28.783 per cent. Ru; extreme difference 0.48, and 41.063 KCl; extreme difference, 0.51. [If K = 39.137, Cl = 35.457; this composition gives Ru = 104.57. The weighings as given in the memoir are misprinted.] Claus also determined the chlorine with silver; the results were such as to show that the salt was not anhydrous, though it had been dried at 200° in an atmosphere of Cl. The salt was prepared by the evaporation of a solution of ruthenium and potassic hydrate in aqua regia, solution of other chlorides of Ru in dilute HCl, and removal of basic compounds by mechanical concentration in water. Claus later takes the atomic weight of Ru = 104. In this memoir he puts it at 651.387 (O = 100,) *104.22* (O = 16,) without mentioning the values of K and Cl. (*Poggend. Ann.*, *65*, 1845, 218.)

SELENIUM.

Regnault determined the specific heat of selenium, which accords with an atomic weight of about 79. (*Gmelin-Kraut*, *l. c.*)

J. J. Berzelius: *79.23* (O = 16).

Berzelius found that 100 Se absorb 179 dry chlorine gas, and that the product was exactly decomposed by water into chlorhydric acid and selenious acid. [If Cl = 35.457 (Stas) the value follows.] (*Poggend. Ann.*, *8*, 1826, 21.)

F. Sacc: *78.55* (O = 16); 490.93 (O = 100).

Sacc's experiments are very discordant. He made three experiments on the reduction of a known weight of selenious acid with ammonium bisulphite and chlorhydric acid. The mean result was Se = 490.38; extreme difference, 5.5. In four experiments barium seleniate was decomposed by heating to redness with sulphuric acid in excess. The salt was found to contain 41.95 selenious acid; extreme difference 0.04. For Ba = 856.877 the resulting value is 491.49. The selenium was purified by solution in nitric acid, evaporation and sublimation, and by reduction with HCl and ammonium bisulphite. Selenious acid was prepared by oxidation with nitric acid. Barium seleniate was prepared by precipitation of barium nitrate with sodium seleniate and heating to redness. Sacc regards 490.3 as the most probable value of Se. (*Annal. de Chim. et de Phys.*, (3,) *31*, 1851, 119.)

A. Schroetter: 78.6 (O = 16).

Details not given. (*Kopp's Jahresbericht*, *4*, 1851, 318; *Sitz.-Bericht der k. k. Acad.*, *6*, 1851, 214.)

Erdmann and Marchand: 78.6 (O = 16); 492.5 (O = 100).

Determined from experiments on mercuric selenide by the same methods employed for the determination of S, q. v. Three experiments gave 71.726, 71.731, 71.741, per cent. mercury. (*Erdmann's Journ. für Prak. Chem.*, *55*, 1852, 202.)

J. Dumas: 76.46 (O = 16).

Determined by seven experiments on the chloridation of selenium. The chloride was condensed in a tube cooled to — 20°, after which the escaping gases were led through other tubes filled with asbestos. The extreme difference in the results was 0.46. Cl = 35.5. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

O. PETTERSSON and G. EKMAN: 79.08 (O = 16).

Determined by five analyses of selenious acid. A warm solution of the acid was acidified with chlorhydric acid, precipitated with sulphurous acid and the selenium collected on a glass filter. Many precautions are necessary in the precipitation and drying. The value is the mean; extreme difference, 0.04. (*Berlin, Bericht der Chem. Gesell.*, *9*, 1876, 1212; *in extenso* in the *Acta of the Scientific Soc. of Upsala.*)

SILICON.

The vexed question of the composition of silicic acid has been settled by H. F. Weber, who found that the specific heat of this element becomes nearly constant above 200° and that the atomic heat is 5.8 for Si = 28. (*Poggend. Ann.*, *154*, 1875, 575.)

J. J. BERZELIUS: *29.63* (O = 16); *185.19* (O = 100).

100 parts of silicon, which had been heated to redness, and freed from silicic acid by hydrofluoric acid, gave 208 parts silicic acid, whence the value. Berzelius also made analyses of barium fluosilicide from which he calculated the oxygen contents of the acid at 51.975. This gives for the atomic weight of Si *29.58*. (*Poggend. Ann.*, *8*, 1826, 20; and *Lehrbuch*, *3*, 1200.)

J. PELOUZE: *28.46* (O = 16); 177.88 (O = 100).

A known weight of perfectly pure silver, dissolved in nitric acid, was brought in contact with a known and slightly excessive weight of silicon tetrachloride and the excess titrated with decimal silver solution. The value is derived from the mean of two experiments; difference 0.76 for O = 100; Cl = 443.2, Ag = 1349.01. The chloride was prepared by Ebelmen; it was perfectly transparent, volatilized without residue, and had been dried for a long time in a vacuum. (*Paris, Comptes Rend.*, *20*, 1845, 1047.)

J. DUMAS: 28.02 (O = 16).

Determined from the mean of two experiments on the tetrachloride which was weighed off in a glass bulb and

introduced, so enclosed, into a vessel containing water. The bulb was broken and the chlorine contents titrated with argentic nitrate. The difference between the experiments was 0.2 for O = 16, Ag = 108, Cl = 35.5. The chloride was repeatedly rectified; its boiling point was 59°. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

J. Schiel: 28.01 (O = 16).

Determined by two analyses of the tetrachloride. The salt was decomposed with a slight excess of ammonium hydrate and the chlorine titrated with argentic nitrate. The atomic weights of Cl and Ag used are not stated. Schiel found 0.6738 silicic chloride = 2.277 argentic chloride, and 1.3092 silicic chloride = 4.418 argentic chloride. [For Ag = 107.93, Cl = 35.457, these data give Si = 28.13, and 27.89.] (*Liebig's Ann.*, *120*, 1861, 94.)

SILVER.

Dulong and Petit, Regnault and others have determined the specific heat of silver and found it in accord with an atomic weight of about 108. (*Gmelin-Kraut*, *l. c.*)

Marcet; Davy; Wenzel; Wollaston.

Wollaston in his table of equivalents mentions that Marcet found 441 Cl = 1350 silver, and Davy the same quantity of chlorine = 1360 silver. Wenzel found 200 sulphur = 1360 silver. (*Phil. Trans.*, *104*, 1814, 21.)

J. J. Berzelius: *108.129* (O = 16); 675.804 (O = 100).

Berzelius found that 100 silver gave 132.75 argentic chloride. Taking Cl = 221.325 he calculates Ag = 1351.607. He expresses uncertainty whether or no this value should not be reduced to one half. (*Poggend. Ann.*, *8*, 1826, 180.)

E. Turner: 108 (O = 16).

Turner determined the composition of argentic chloride at 100 silver to 132.8 chloride. These numbers are for

vacuum. If $Cl = 35.42$ (Turner) the value follows. (*Phil. Trans.*, *123*, 1833, 536.)

F. PENNY: 107.97 ($O = 16$).

Penny made six experiments on the conversion of silver into nitrate. The silver was dissolved in cold nitric acid, the solution evaporated, and the nitrate fused all in one flask and with precautions against loss by spiriting. He found 100 $Ag = 157.441$ nitrate; extreme difference, 0.028. In five experiments the nitrate from the preceding determinations was converted into chloride, by means of chlorhydric acid, in the same flask, dried, fused, and weighed. Penny could detect no decomposition in fusion. He found 100 $Ag = 132.8372$ chloride; extreme difference, 0.01. In two experiments silver was dissolved in nitric acid, precipitated with chlorhydric acid, evaporated and fused, giving 132.830 and 132.838. The mean of all seven experiments is 132.836. Penny takes 132.837. From the relations of the chlorides, chlorates, and nitrates of potassium and sodium, Penny had determined the difference between the atomic weights of a chloride and a nitrate at 26.565. This gives the molecular weight of argentic chloride at 143.424 and $Ag = 107.97$. The silver used, as well as the water and the acids, were carefully tested for impurities and a minute amount of solid residue in the twice distilled water and in the acids was allowed for. The weighings were all reduced to vacuum. (*Phil. Trans.*, *129*, 1839, 27.)

C. MARIGNAC: *108* ($O = 16$); 675 ($O = 100$).

Silver was dissolved in nitric acid and precipitated with chlorhydric acid. One experiment, reduced to vacuum, gave 100 silver = 132.74 chloride, which Marignac considered confirmatory of Berzelius' value, 132.75. He therefore adopted the latter number. 100 potassic chloride were found to produce 192.26 argentic chloride, in two experiments, the difference between which was 0.01. By analysis, by means of heat, of potassic chlorate, Marignac had found the molecular weight of the chloride 932.14, these relations give the molecular weight of argentic chloride at 1792.13 and the atomic weight of silver at 1350. The potassic chloride was prepared by heating the chlorate and cooling the resulting chloride over sulphuric acid. (*Liebig's Ann.*, *44*, 1842, 23.)

C. MARIGNAC: *107.922* (O = 16); 674.505 (O = 100).

Marignac redetermined the relation between silver and potassic chloride by Pelouze's method. He found 100 Ag = 69.062 KCl in six experiments, the extreme difference between which was 0.018. In five experiments he found 100 KCl = 192.348 Ag; extreme difference 0.04. He also redetermined the composition of argentic chloride. The silver was dissolved in a long-necked flask and the fumes passed into a second flask containing water. Solution being effected, the water from the second flask was added to the contents of the first, and the whole precipitated with HCl. The chloride was washed, dried, melted and weighed in the same flask. The result was 100 Ag = 132.84 chloride; extreme difference 0.019. Combination of these data with Marignac's old value for the molecular weight of KCl, 932.14, gives Ag = 1349.01. All weighings reduced to vacuum. Berzelius revised the result by throwing out one experiment and by rejecting the correction for vacuum. He thus got Ag = 1349.66. (*Berzelius' Jahresbericht, 24*, 58; *25*, 31; *Bibl. Univ. de Genève*, *46*, 1842, 350.)

In opposition to Prout's hypothesis, Marignac cites his analyses of argentic acetate, in which the escaping gases were forced to pass over porous silver. They gave in three experiments 64.664 silver from 100 acetate; extreme difference 0.005. If C = 75, this gives Ag = 1349.6. He also found 100 Ag = 157.455 nitrate. [If N = 87.5, this gives Ag = 1348.88.] He also found 100 Ag = 49.556 ammonium chloride. (*Liebig's Ann.*, *59*, 284; *Bibl. Univ. de Genève*, 1846.)

LIEBIG and REDTENBACHER; STRECKER: *107.903* (O = 16); 674.395 (O = 100).

Strecker recalculated Liebig and Redtenbacher's analyses of argentic acetate, tartrate, racemate and malate by the method of least squares, and from the difference in the atomic composition of these salts. He obtained for Ag the value 1348.79. *Vide* Carbon. (*Liebig's Ann.*, *59*, 1846, 280.)

E. J. MAUMENÉ: *108.026* (O = 16); 675.16 (O = 100).

In four experiments argentic oxalate was mixed with sand in a flask and decomposed by heat in a current of air. The

products of decomposition were passed over cupric oxide, and through drying tubes and potash tubes. In five experiments the acetate was treated in the same way, but not mixed with sand. The mean result was Ag = 1350.32; extreme difference 0.77. Maumené found it very difficult to purify the oxalate, which showed traces of nitric acid after 100 washings. (*Annal. de Chim. et de Phys.*, (3,) *18*, 1846, 41.)

J. S. Stas: 107.93 (O = 16).

Thirteen syntheses of argentic iodide, performed by bringing hydroiodic acid in contact with argentic sulphate or nitrate, gave 100 Ag = 117.5343 iodine. Three analyses of argentic iodate, performed by decomposition by heat in a current of nitrogen or by reduction of the salt, while in suspension, by a current of sulphurous anhydride, gave AgI = 234.779. Hence Ag = 107.928. Four syntheses of the bromide, performed by bringing hydrobromic acid in contact with argentic sulphate, gave 100 Ag = 74.0805 Br. Two analyses of argentic bromate, by reduction while in suspension with sulphurous anhydride, gave Ag Br = 187.87. Hence, Ag = 107.921. Seven syntheses of argentic chloride, three of them by combustion of silver in chlorine, three by precipitation with HCl, and one by precipitation with ammonium chloride, gave 100 Ag = 32.8445 Cl. Stas adopts the number 32.85 on the supposition that no excess of chlorine was possible. The chloride was fused. Two analyses of the chlorate, accomplished by heat or by evaporation with chlorhydric acid, gave Ag Cl = 143.395. Hence Ag = 107.937. Five syntheses of the sulphide, performed by heating silver in a current of sulphur vapor, or of hydrogen sulphide, gave 100 Ag = 114.8522 argentic sulphide. Six analyses of the sulphate by reduction in a current of hydrogen, showed that 100 sulphate contained 69.203 silver, hence Ag =107.920, [107.926? *vide* Sulphur.] From analysis of potassium chlorate, Stas had determined the molecular weight of KCl at 74.59. By twenty-four determinations he found 100 Ag = 69.103 KCl, hence Ag = 107.943. The silver was prepared either by Levol's method or by decomposing an ammoniacal solution of argentic nitrate with a mixture of ammonium sulphite and a copper salt. The metal was heated to the boiling point until the sodium line disappeared and the metallic fumes were a pale blue. To test its purity, it was compared with distilled silver. See Stas's determinations of Cl, Br, I, S,

and K. All weighings reduced to vacuum. (*Stas, Untersuch. über Chem. Prop., Leipzig*, 1867.)

SODIUM.

The specific heat of sodium has been determined by Regnault and indicates an atomic weight of about 23. (*Gmelin-Kraut, l. c.*)

H. Davy; F. H. Wollaston: *23.28* (O = 16); 145.5 (O = 100).

Davy found that 134 Cl combine with 88 Na to form sodium chloride. If Cl = 441, the value follows. (*Phil. Trans., 104*, 1814, 20.)

J. J. Berzelius: *23.164* (O = 16).

Berzelius found that 100 Na Cl = 244.6 Ag Cl. [If Ag Cl = 143.387, (Stas,) the value follows.] (*Poggend. Ann., 8*, 1826, 189.)

F. Penny: 23.046 (O = 16).

Penny made four experiments on the conversion of the chlorate into the chloride by means of HCl. A known weight of the salt was dissolved in a flask in the acid and evaporated, dried and weighed without removal. The sodium chloride was not fused. The mean result was that 100 chlorate equals 54.930 chloride; extreme difference, 0.02. This relation gives the molecular weight of the chloride at 58.5. Penny had found the atomic weight of Cl = 35.454; hence the value for Na. [If Cl = 35.457 (Stas,) Na = 23.043. Stas himself found 23.043.] The sodium chlorate was prepared by precipitating potassium chlorate with sodium bitartrate, and purifying the sodium chlorate by recrystallization. The weighings are for vacuum. (*Phil. Trans., 129*, 1839, 25.)

J. Pelouze: *22.97* (O = 16); 143.59 (O = 100).

A known weight of perfectly pure silver was dissolved in nitric acid, and brought in contact with a known and

slightly excessive weight of sodium chloride, and the excess titrated with decimal silver solution. The mean result of three experiments was that 100 Ag = 51.141 Na Cl; extreme difference, 0.033. The value follows for Ag = 1349.01; Cl = 443.2. The sodium chloride was prepared either from sodium sulphate and barium chloride, or from sodium carbonate and chlorhydric acid, or from a very pure rock salt. It was repeatedly recrystallized and was dried at 200° or melted. (*Paris Comptes Rend.*, *20*, 1845, 1047.)

J. DUMAS: 23.011 (O = 16).

Determined from the mean of seven experiments on the titration of sodium chloride with argentic nitrate; extreme difference, 0.09. Ag = 108; Cl = 35.5 [Dumas gives the mean as 23.014 instead of 23.0114.] For five experiments Na Cl recrystallized ten times and melted was employed. For two experiments (giving an average of 23.036) the residue from the incineration of the acetate was used to prepare Na Cl, which was recrystallized four times and melted. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

J. S. STAS: 23.043 (O = 16).

According to the mean of 10 determinations 100 Ag = 54.2078 Na Cl; extreme difference 0.0033. The sodium chloride was found to contain a minute quantity of silicic acid which reduces the result from Na = 23.049 to 23.045 for Ag = 107.93; Cl = 35.457. According to the mean of five determinations 100 Na Cl = 145.4526 sodium nitrate; extreme difference 0.025. If N = 14.044 this gives Na = 23.045. The lowest determination gives Na = 23.042. The sodium chloride was purified by recrystallization and in part by conversion into sodium chloroplatinate. The weighings are for vacuum. (*Stas*, *Untersuch. über Chem. Prop.*, *Leipzig*, 1867.)

STRONTIUM.

Regnault determined the specific heat of strontium chloride. It corresponds to an atomic weight of about 87.5. (*Gmelin-Kraut*, *l. c.*)

M. H. KLAPROTH; F. H. WOLLASTON: *94.4* (O = 16); 590 (O = 100).

Klaproth found 42 sulphuric anhydride = 58 strontium oxide; whence the value for S = 200. (*Phil. Trans.*, *104*, 1814, 20.)

F. STROMEYER; *87.34* (O = 16); 545.929 (O = 100).

According to Berzelius, Stromeyer found that 100 strontium chloride = 181.25 argentic chloride; whence the value, for Ag = 1349.66; Cl = 221.64. (*Berzelius' Lehrbuch*, *3*, 1229.) In *Gilbert's Ann.*, *54*, 1816, 251, Stromeyer refers to this analysis as by V. Rose. Stromeyer himself found 0.5 grm. carbonate = 75.5394 c. c. carbon di-oxide [which gives Sr = 88.26 if 1000 c. c. carbon di-oxide weigh 1.96433 grm.] Stromeyer calculated Sr = 552.28 for O = 100.

—. SALVETAT: 88 (O = 16); 550 (O = 100).

Determined from the loss of weight of strontium carbonate by calcination and on driving off carbon di-oxide with sulphuric acid. Details not given. (*Paris Comptes Rend.*, *17*, 1843, 318.)

J. PELOUZE: *87.68* (O = 16); 548.02 (O = 100).

A known weight of perfectly pure silver was brought in contact with a known and slightly excessive amount of strontium chloride and the excess titrated with decimal silver solution. The number is the mean of two experiments; extreme difference, 0.2. Ag = 1349.01; Cl = 443.2. The chloride was purified by recrystallization and was dried at 200° or below redness. (*Paris Comptes Rend.*, *20*, 1047.)

C. MARIGNAC: 87.54 (O = 16).

Marignac made experiments on three different preparations of strontium chloride, (1,) (2,) (3.) Compared with silver by Pelouze's method it was found that ten grammes strontium chloride = (1) 8.103; (2) 8.099; (3) 8.101 silver. The same strontium chloride converted into sulphate gave (1) 6.887; (2) 6.8855; (3) 6.884 sulphate. In both these series of experiments the strontium was weighed as air-dried, hydrous, crystalline chloride. Comparison gives Sr

= (1) 43.79; (2) 43.82; (3) 43.77. In each experiment of the latter series the water was determined by driving it off at a red heat. It was proved that the chloride does not undergo decomposition at this temperature, and the water contents was found to vary no more than 0.0005 of the total weight. In three more experiments the water was determined, and the anhydrous salt analysed by Pelouze's method giving (1) 43.77; (2) 43.74; (3) 43.76. Ag = 108; Cl = 35.5; S = 16. The chloride was prepared (1) from the chemically pure chloride of commerce by precipitating barium with sulphuric acid, separation of lime by precipitation of the strontium chloride by HCl gas and washing with chlorhydric acid. The purity was tested by the solubility of a portion converted into sulphate. The chloride was finally redissolved and precipitated with alcohol. (2) was prepared from (1) by a repetition of the same process. (3) was prepared from (2) by recrystallization. (*Bibl. Univ., Arch. des Sciences*, (2,) *1*, 1858, 220.)

J. Dumas: 87.52 (O = 16).

Determined from the mean of six experiments on the analysis of strontium chloride with argentic nitrate. The extreme difference was 0.14, Cl = 35.5; Ag = 108. The salt was purified by boiling with sulphuric acid, and precipitation with and recrystallization from chlorhydric acid. These processes were in some cases several times repeated. The pure salt was fused in a current of HCl gas. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

SULPHUR.

Deville and Troost and others have determined the density of sulphur in the gaseous form. It corresponds to an atomic weight of about 32. The specific heat of sulphur also agrees moderately well with this value. (*Gmelin-Kraut, l. c.; L. Meyer, l. c.*)

J. J. Berzelius; F. H. Wollaston: *32* (O = 16); 200 (O = 100).

According to Wollaston, Berzelius found that plumbic sulphide was composed of 86.64 lead and 13.36 S. Hence the value, for lead = 1295. (*Phil. Trans.*, *104*, 1814, 20.)

J. J. BERZELIUS : *32.19* (O = 16) 201.165 (O = 100).

A known weight of lead was dissolved in pure nitric acid, precipitated with sulphuric acid and evaporated. The mean result of four experiments was that 100 Pb = 146.44 sulphate. The variation was only in the fifth figure. If lead = 1294.498 the value follows. [If this relation is recalculated with Stas's atomic weight of lead, S = 32.096.] (*Poggend. Ann. 8*, 1826, 16.)

E. TURNER : 32.17 (O = 16).

Determined from syntheses of plumbic and baric sulphates. The former gave 16.083, the latter, 16.087. Ba = 68.7, Pb = 103.6. The numbers are for vacuum. *Vide* Barium and Lead. (*Phil. Trans.*, *123*, 1833, 539.)

T. THOMSON : *32* (O = 16); 200 (O = 100).

This chemist found the specific gravity of sulphurous acid in mean of two experiments, 2.22216, almost exactly double 1.1111 which he takes (on utterly untenable grounds) for the specific gravity of oxygen. (*Erdmann's Journ. für Prak. Chem.*, *8*, 1836, 370; *Records of General Science by R. D. Thomson*, 1836, 179.)

ERDMANN and MARCHAND : *32.004* (O = 16); 200.026 (O = 100).

Determined by four experiments on the decomposition of mercuric sulphide by copper, in a current of carbon dioxide, the mercury being caught in a cold receiver. The mean composition was found to be for vacuum 86.211 mercury and 13.789 sulphur, extreme difference, 0.017 Hg. If Hg = 1250.6, the value follows. In purifying the sulphide it was first heated to drive off excess of sulphur and then sublimed three times, the first and last portions of the sublimate being rejected. (*Erdmann's Journ. für Prak. Chem.*, *31*, 1844, 396.)

J. J. BERZELIUS : *32.12* (O = 16); 200.75 (O = 100).

Berzelius' former value, 201.165, is changed by the new value for lead, 1294.645 to 200.8017. Three new experiments were made by gently heating argentic chloride in a current of hydrogen disulphide. The mean of three experiments gives S = 200.706; extreme difference 0.11. Cl = 443.38, Ag = 1349.66. (*Berzelius' Jahresbericht*, *25*, 1845, 37, and *Lehrbuch*, *3*, 1185.)

H. Struve: 32.002 (O = 16).

Determined by six experiments on the reduction of a known weight of argentic sulphate in a current of hydrogen. The number is the mean; extreme difference, 0.146. Ag = 108. The sulphate was prepared by precipitating the nitrate with an excess of sulphuric acid, and drying at a high temperature. (*Liebig's Ann.*, *80*, 1851, 203; *Berzelius' Jahresbericht*, *30*, 20.)

J. Dumas: 32.0196 (O = 16).

Determined by five experiments on the combustion of silver in sulphur vapor. The number is the mean; extreme difference, 0.054. Ag = 108. The sulphur was purified by repeated distillation. The silver was heated to redness in a current of sulphur vapor, the excess of sulphur being afterwards distilled off in a current of carbon di-oxide. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 147.)

J. S. Stas: 32.0742 [?] (O = 16).

According to the mean of six analyses of argentic sulphate by decomposition in a current of hydrogen at as low a temperature as possible, 100 sulphate yield 69.203 [more exactly 69.20317] silver; extreme difference, 0.012. Five syntheses of the sulphide, performed by heating silver in a current of sulphur vapor or hydrogen disulphide, showed that 100 silver = 114.8522 sulphide; extreme difference, 0.005. By comparing these figures, which are for vacuum, Stas deduces S = 32.0742; Ag = 107.920. [There seems to be a trifling error in this calculation. The weighings seem to be correct, for the means correspond to the details given. As given, the numbers indicate S = 32.058; Ag = 107.926. The latter is almost identical with Stas's mean value, 107.930.] The sulphate was prepared by the action of sulphuric acid on argentic nitrate, or by solution of silver in sulphuric acid. The salt was heated above the boiling point of sulphuric acid. (*Stas, Unters. über Chem. Prop., Leipzig*, 1867.)

TANTALIUM.

Deville and Troost have determined the vapor density of tantalium chloride. It agrees with an atomic weight of 182. (*Paris Comptes Rend.*, *64*, 1867, 294.)

J. J. BERZELIUS : *167.74* (O = 16).

Berzelius decomposed the sulphide in dry chlorine gas and decomposed the resulting chloride with water. 99.75 parts sulphide yielded 89.35 tantalic acid. On the supposition that the acid contains three atoms of oxygen Berzelius calculates the atomic weight at 1148.365 for S = 200.75. [If the acid contains five atoms of oxygen the value becomes 167.74.] (*Poggend. Ann.*, *4*, 1825, 14, and *Lehrbuch*, *3*, 1209.)

Rose denies that the sulphide formed, as Berzelius prepared it, by heating tantalium in carbon disulphide vapor is a constant compound. (*Poggend. Ann.*, *99*, 580.) Marignac, however, shows that Berzelius, Rose and Hermann, obtained constant results from its analysis, from 89.50 to 90 acid from 100 sulphide. If Ta = 182, the sulphide would give 90.24 acid. (*Liebig's Ann.*, *S*, *4*, 1866, 358.)

H. ROSE : *172* (O = 16).

Out of twelve analyses of the chloride, in which both the chlorine and the tantalic acid were determined, Rose selected two in which the agreement was best. [These analyses calculated for Ag = 107.93, Cl = 35.457, give Ta = 171.96.] The chloride was prepared from tantalic acid especially freed from tungsten and tin by mixing with carbon, drying in carbon di-oxide, and heating in a current of chlorine in which the salt was allowed to cool. Excess of chlorine was expelled by dry air, and the salt was hermetically sealed in glass. Rose supposed the acid to contain two atoms of oxygen and therefore deduces the value 859.81 (O = 100). (*Poggend. Ann.*, *99*, 1856, 75.)

Marignac seems to prove that the material with which Rose dealt contained niobium. He states that the chlorides of the two elements cannot be separated from one another, and that there are no characteristics by which their purity can be decided. (*Liebig's Ann.*, *S*, *4*, 1866, 352.)

R. HERMANN:

Hermann made many analyses of tantalium salts to which, however, he ascribes quite incomprehensible formulas. Marignac has shown that his methods were utterly inadequate to produce pure preparations. He assumes two atoms of tantalium and three atoms of oxygen in the acid and gives the atomic weight as 645. ($O = 100$.) (*Erdmann's Journ. für Prak. Chem.*, *70*, 1857, 193.)

C. MARIGNAC: 182 ($O = 16$).

Berzelius', Rose's and Marignac's analyses of the double fluoride of tantalium and potassium show that the fluorine is combined with Ta and potassium in proportions of two to five. The salt has also exactly the crystal form of the niobium salt. Hence the acid is a ditantalic pentoxide. Four experiments were made on this salt by drying at 100°, moistening with sulphuric acid and heating gradually till the excess of acid was driven off. The potassic sulphate was leached out, evaporated, melted and weighed, and the tantalic acid heated to redness and weighed. The mean potassic sulphate contents was found to be 44.29 per cent; extreme difference, 0.15. The mean amount of tantalic acid obtained was 56.59; extreme difference, 0.25. If $K = 39$, these data give $Ta = 182.3$. Four analyses were also made of the ammonium salt. This contained traces of potassium which were determined and allowed for in each case. The mean amount of tantalic acid obtained was 65.25 per cent; extreme difference, 0.34. This gives $Ta = 182$, the number which Marignac adopts. The salts were obtained by dissolving tantalic acid, which had not been heated to redness, in fluohydric acid, adding potassic or ammonic hydrate and purifying by recrystallization. These salts are much less soluble than the corresponding niobium and titanium salts. (*Liebig's Ann.*, *S. 4*, 1866, 234.)

TELLURIUM.

Regnault and Kopp have each determined the specific heat of tellurium and found it in accord with an atomic weight of about 128. (*Gmelin-Kraut*, *l. c.*)

J. J. BERZELIUS *129.03* (O = 16); 806.452 (O = 100).

A known weight of metallic tellurium was oxidized with nitric acid, the excess of acid being driven off by heat. It was found that 100 Te gave 124.8 tellurious acid. (*Poggend. Ann.*, *8*, 1826, 24.)

J. J. BERZELIUS: *128.28* (O = 16); 801.76 (O = 100).

Determined as before but with purer material. Three experiments were made, which gave 802.838, 801.786, 801.74. Berzelius took the mean of the latter two. The tellurium was prepared from tetradymite by heating with potassium carbonate and olive oil in a closed crucible, dissolving the potassium telluride so formed in water free from air, precipitating the tellurium by a current of air and distilling it in a current of hydrogen. (*Poggend. Ann.*, *32*, 1834, 16.)

K. VON HAUER: 128.06 (O = 16).

Determined from the mean of five experiments on the precipitation of bromine with argentic nitrate from the double bromide of potassium and tellurium. The bromine contents was found to be 69.9236 per cent., for Ag = 108.1; Br = 80; extreme difference 0.172. If K = 39.2, the value follows. The salt was prepared by mixing tellurium and potassic bromide in atomic proportions, adding water and bromine, heating to drive off excess of bromine and repeated recrystallization. (*Erdmann's Journ. für Prak. Chem.*, *73*, 1858, 98; *Sitz-Bericht der k. k. Acad.*)

J. DUMAS: 129 (O = 16).

No details are given. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 129.)

THALLIUM.

Regnault determined the specific heat of thallium. It agrees with an atomic weight of 204. (*Gmelin-Kraut*, *l. c.*)

A. LAMY: 204 (O = 16).

Three analyses of the chloride with argentic nitrate gave

a mean of 204; extreme difference 1.2. An experiment on the precipitation of the sulphate with barium nitrate gave 204.3. [The atomic weights used were probably those accepted by Dumas.] The salts were purified by recrystallization. (*Annal. de Chim. et de Phys.*, (3,) *67*, 1863, 411.)

W. CROOKES: 202.96 (O = 16).

These determinations were made from the sulphate, which was prepared with great care. By decomposing the sulphate with potassic iodide and weighing the thallic iodide formed, the atomic weight was found at 202.73; by precipitation with barium nitrate, 203.55; with chlorhydric acid and alcohol, thallic chloride being weighed, 201.85; from the amount of sulphate produced from a known weight of metal, 203.1; by precipitation with platinum chloride, 203.56. The values taken for Cl, I, etc., are not given; [they were probably those accepted by Dumas.] (*Erdmann's Journ. für Prak. Chem.*, *92*, 1864, 277; *Chem. News.*)

H. WERTHER: 204 (O = 16).

In five experiments Werther decomposed thallic iodide with potassic hydrate and zinc, both perfectly pure, and precipitated the iodine with silver. The mean result of these experiments was Tl = 204.4; extreme difference 1.7. [The value assumed for I is not stated. One experiment, which gave exactly 204, according to Werther, recalculated for Ag = 107.93; I = 126.85 gives Tl = 203.63.] Three experiments were made by decomposing the iodide with ammoniacal solution of argentic nitrate and weighing the argentic iodide formed. These determinations gave Tl = 203.47; extreme difference 0.3. The preparation of the iodide is not given. (*Erdmann's Journ. für Prak. Chem.*, *92*, 1864, 136.)

M. HEBBERLING: 203.94 (O = 16).

Hebberling made three experiments on the sulphate by precipitation with barium chloride, which gave in mean Tl = 204.13; extreme difference 0.2. He also made two experiments on the chloride by precipitation with argentic nitrate. These gave 203.8 and 203.5. The atomic weights assumed are not stated. [If Ag = 107.93; Cl = 35.457; the first analysis of the chloride gives Tl = 203.44. The data for the second analysis are misprinted. If a probable correction of a single figure is made, the data give Tl =

203.026.] The salts were purified by recrystallization. (*Liebig's Ann.*, *134*, 1865, 11.)

W. CROOKES: *204.155* (O = 16).

Determined by experiments on the solution of metallic thallium in nitric acid and evaporation to dryness. The number is the mean of ten experiments; extreme difference, 0.038. The balance stood in a partial vacuum, and the weighings were made at two different pressures and calculated for vacuum. Very elaborate precautions were taken throughout. Crookes also mentions determinations made with barium nitrate, but gives no data. The thallium was prepared in seven different lots by the reduction of as many different salts which had been purified by recrystallization &c. The metal was fused in lime. The reagents were expecially prepared by methods similar to those of Stas. Crookes took N = 14.009, O = 15.96, and calculated for Tl the value 203.642. [If O = 16, the value becomes 204.155.] (*Phil. Trans.*, *163*, 1873, 277.)

THORIUM.

From the isomorphism existing between thorium, tin, and titanium, and from the similarity of thorium to zirconium, Delafontaine and Marignac believe the oxide to contain two atoms of oxygen. (*Liebig's Ann.*, *131*, 100.) Neither the specific heat of this element nor the vapor density of any of its compounds has been determined so far as I know.

J. J. BERZELIUS; *238* (O = 16); 1887.72 (O = 100).

From the sulphate, precipitated by heating a solution of the salt and redissolved in cold water, Berzelius got the values 748.493 and 735.713 by precipitating with barium chloride. He also analysed the double sulphate of potassium and thorium. From the relation between the sulphuric acid and the thorium oxide found, the atomic weight would seem to be 750.63, while the relation between the potassic sulphate obtained, and the amount of oxide gives 740.6. These numbers are calculated on the supposition that the oxide contains a single atom of oxygen. Ba =

855.29, S = 200.75, K = 488.856. (*Poggend. Ann.*, *16*, 1829, 398, and *Lehrbuch*, *3*, 1224.)

J. J. Chydenius: 236.64 (O = 16).

This chemist analysed the sulphate, the double sulphate of potassium and thorium, the oxalate, the acetate and the formate, getting results which vary from 228.52 to 243.76. He averages with his own results analyses made by Berzelius and by Berlin, which, however, alter the result inappreciably. According to Delafontaine, the methods employed for purification are ineffectual. Chydenius assumes a single atom of oxygen in the oxide. (*Poggend. Ann.*, *119*, 1863, 55.)

N. J. Berlin: 231.64 (O = 16).

Chydenius reports two analyses of the oxalate by Berlin which gave for thorium 57.87 and 57.95, or 231.48 and 231.80. (*Poggend. Ann.*, *119*, 1863, 56.)

M. Delafontaine: 231.5 (O = 16).

Determined from analyses of the sulphate. Fourteen experiments on the decomposition of this salt, by the heat of a strong double-draught lamp, gave a mean of 52.51 per cent. oxide; extreme difference, 0.83. In three experiments the sulphur contents of the salt was determined by precipitation with barium chloride after the sulphate had been decomposed with ammonium oxalate. The mean amount of sulphuric anhydride so found was 31.92 per cent.; extreme difference, 0.78. Three experiments on the water contents gave 15.68 per cent; extreme difference, 0.21. The sum of these means is 100.11. The value of thorium was calculated from the relation of the oxide to the sulphuric anhydride for S = 32, Ba = 137. The salt was prepared from thorite and from orangite by decomposition with sulphuric acid and recrystallization of the sulphate with the help of heat. The purification was continued until the crystals and the mother liquor had exactly the same composition. Marignac assisted at this investigation. (*Liebig's Ann.*, *131*, 1864, 100.)

P. T. Cleve: 233.88 (O = 16).

Cleve made six analyses of the anhydrous sulphate, getting in mean Th = 233.8; extreme difference, 1.36. From

analyses of the oxalate he got 233.97; extreme difference, 0.6. (*Kopp's Jahresbericht*, 1874, 261; *Bull. Soc. Chim.*, (2,) *21*, 116.)

TIN.

Regnault and Kopp have each determined the specific heat of tin. It agrees with an atomic weight of about 118. Dumas, Cahours and others have determined the vapor density of volatile tin compounds with a similar result. (*Gmelin-Kraut, l. c.; L. Meyer, l. c.*)

J. J. BERZELIUS; *117.647* (O = 16); 735.294 (O = 100).

Berzelius determined this value by oxidizing pure tin foil by means of nitric acid and weighing the oxide. He found 100 tin = 127.2 stannic acid. (*Poggend. Ann.*, *8*, 1826, 184.)

G. J. MULDER: 116.112 (O = 16); 725.7 (O = 100).

Two experiments were made by oxidizing tin with nitric acid, evaporating, drying, and heating to redness. They gave each 100 tin = 127.56 stannic acid; whence the value. All possible precautions are said to have been taken. The metal was prepared by the reduction of pure oxide with soot and a flux. (*Erdmann's Journ. für Prak. Chem.*, *48*, 1849, 35; *Scheikundige Onderzoek.*, 5. *Deel*, 260.)

C. L. VLAANDEREN: about 118. (O = 16).

Determined from experiments on the oxidation and reduction of tin and stannic acid in vessels of various materials. The experiments regarded as the most accurate were made on the reduction of the acid in a current of hydrogen in porcelain vessels. The acid had been heated in platinum. These experiments gave 59.04 and 59.12. Stannic acid heated in glass or porcelain was found to retain nitric acid. (*Kopp's Jahresbericht*, *11*, 1858, 138; *Mulder, Scheikundige Verh. en Onderzoek.*, 2. *Deel*, 150.)

J. DUMAS: 118.08 (O = 16).

Two experiments were made on the oxidation of pure tin by nitric acid. The stannic acid being heated white

hot in platinum vessels gave for the atomic weight 59.1 and 58.96. The tin employed was prepared from pure chloride. Two experiments on the titration of the chloride with argentic nitrate gave 59.06 and 59.03. Ag = 108, Cl = 35.5. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 156.)

TITANIUM.

The specific heat of titanic acid has been determined by Regnault and by Kopp, and indicates an atomic weight of about 50. Dumas determined the vapor density of the tetrachloride at 6.836. [If the molecular weight of O = 32, and if Cl = 35.457, this gives Ti = 56.025.] (*Gmelin-Kraut*, *l. c.*, and *Poggend. Ann.*, *9*, 1827, 441.)

H. Rose: *61.17* (O = 16).

Determined by roasting titanium sulphide and weighing the titanic acid formed. The highest result obtained was 1.017 sulphide from 0.757 acid. This result Rose adopted on the supposition that an excess was impossible. For S = 201.16 these data give Ti = *62.25* (O = 16); 389.1 (O = 100.) [If S = 32, Ti = 61.17.] The sulphide was prepared by heating titanic acid in a current of carbon disulphide. (*Gilbert's Ann.*, *73*, 1823, 135.)

Rose subsequently expressed the opinion that the sulphide employed in this analysis was impure, and contained undecomposed titanic acid, but afterwards came to the conclusion that it was perfectly pure, accounting for the variation of the results from those he obtained later by the theory that the sulphide and the oxide of this element, like those of tantalium, were entirely dissimilar compounds. Marignac has shown that tantalium sulphide is of normal constitution. (*Poggend. Ann.*, *99*, 1856, 576.)

H. Rose: 48.28 (O = 16).

Titanium chloride was decomposed with water, titanic acid precipitated by ammonic hydrate, and the chlorine precipitated from the filtrate with argentic nitrate. Taking Ag = 1351.607, Cl = 221.325; Rose calculated the chlorine contents in four experiments at from 74.43 to 74.53 per

cent; mean 74.46 and Ti at 303.686. According to Gmelin-Kraut, these analyses recalculated for Stas's values give Ti = 48.28. The chloride was prepared by the action of chlorine on a mixture of titanic acid and carbon, and was rectified four or five times over potassium and mercury. It was clear and developed no chlorine on decomposition with water. (*Poggend. Ann.*, *15*, 1829, 145.)

C. G. Mosander: *47.33* (O = 16); 295.81 (O = 100).

Mosander determined the oxygen contents of titanic acid at from 39.83 to 40.82 per cent.; mean 40.427. Mosander never described the method of analysis. [The oxygen contents was probably determined from the chloride, for the above data give Ti = 294.7, while Berzelius records the determination as having given 295.81.] (*Poggend. Ann.*, *19*, 1830, 212, and *Berzelius' Lehrbuch*, *3*, 1211.)

J. Pierre: *50.36* (O = 16).

Determined by three experiments on the titration of the chloride with argentic nitrate by Pelouze's method. Pierre does not give the values taken for Cl and Ag. He calculates the atomic weight of Ti at 314.69. [If Ag = 107.93, Cl = 35.457; his data give Ti = 314.75 (O = 100); 50.36 (O = 16), with an extreme difference in the latter case of 0.08.] He made two other determinations giving lower results, but it was found that the chloride employed was slightly decomposed by contact with air. The chloride was prepared from artificial titanic acid which was free from iron, and was further purified by fractional distillation. (*Annal. de Chim. et de Phys.*, (3,) *20*, 1847, 257.)

A. Demoly: *56.512* (O = 16).

Determined by experiments on the tetrachloride. The salt was decomposed with water, the titanic acid precipitated by ammonic hydrate, and the chlorine precipitated in the filtrate, after the excess of ammonic hydrate had been volatilized and the solution acidified. Both precipitates were weighed. Demoly calculates the atomic weight of Ti at 350, without mentioning what values he accepted for silver and chlorine. [If Ag = 107.93, Cl = 35.457; the atomic weight, calculated from the argentic chloride, is 353.2 (O = 100); or 56.512 (O = 16), with an extreme difference in the three experiments of 0.88 for O = 16.] The chloride was prepared from rutile by preliminary conver-

sion into nitride, &c. It was purified by rectification over mercury and potassium. (*Liebig's Ann.*, *72*, 213; *Laurent and Gerhardt*, *Comptes Rend.*, 1849, 325.)

TUNGSTEN.

Regnault has determined the specific heat of tungsten, and Roscoe the vapor density of the chloride. These experiments place the atomic weight of tungsten at about 184. (*Gmelin-Kraut*, *l. c.*; *L. Meyer*, *l. c.*)

J. J. Berzelius: *189.26* (O = 16); 1183.355 (O = 100).

A weighed quantity of tungstic acid was reduced in a current of hydrogen, again weighed, then re-oxidized and reweighed. The number is the mean result of the two operations. The number is given in Berzelius' *Lehrbuch* as 1188.36 with the data, which are also given in *Poggend. Ann.*, *8*, 23. It is pointed out in *Graham-Otto* that this value must be misprinted, an observation which I have verified. (*Poggend. Ann.*, *4*, 1825, 152.)

Berzelius made an earlier determination than the foregoing by the oxidation of the sulphide, getting 1207. He points out the source of error in this experiment arising from the formation of irreducible sulphate. (*Berzelius' Jahresbericht*, *5*, 1825, 121.)

R. Schneider: 184.12 (O = 16); 1150.78 (O = 100).

Schneider made five experiments on the reduction of tungstic acid with hydrogen in a porcelain tube heated by a charcoal fire. These analyses gave the mean contents of the acid at 79.316 tungsten per hundred; extreme difference, 0.096. This composition corresponds to an atomic weight of 1150.39. He also made three experiments on the combustion of tungsten, getting a mean of 79.327 tungsten per 100 acid; extreme difference, 0.005, or an atomic weight of 1151.17. The value taken is the mean. The tungstic acid was prepared by decomposing ammonio-tungstic sulphide with chlorhydric acid, washing the precipitate with acid, solution in ammonia, reprecipitation with chlorhydric acid, and so on until a perfectly pure product was obtained. The tungstic acid was finally dried and

heated to redness. (*Erdmann's Journ. für Prak. Chem.*, *50*, 1850, 163.)

R. F. Marchand: *184.1* (O = 16); 1150.6 (O = 100).

Determined from two experiments on the reduction of tungstic acid in a current of hydrogen, and two experiments on the combustion of tungsten. These determinations were made in the same manner as and at the same time with Schneider's. The extreme difference was 3.5 for O = 100. (*Liebig's Ann.*, *77*, 1851, 263.)

J. B. von Borck: *183.816* (O = 16); 1148.85 (O = 100).

Determined by seven experiments on the reduction of tungstic acid at a white heat by hydrogen, and by two experiments on the combustion of tungsten. The number is the mean; extreme difference, 10.38 for O = 100. The tungstic acid was prepared from Wolframite by fusing the mineral with potassium carbonate, solution in water containing alcohol, precipitation with calcic chloride and decomposition of the calcic tungstate with chlorhydric acid. The tungstic acid so produced was converted into ammonium salt which, on decomposition, yields a compound free from iron and manganese. (*Erdmann's Journ. für Prak. Chem.*, *54*, 1851, 254.)

A. Riche: 174 (O = 16).

This value was reached by five determinations of the amount of water produced by the reduction of tungstic acid in a current of hydrogen, which gave a mean of 87.07; extreme difference, 1.78. The tungstic acid was obtained by heating the ammonium salt, or by the decomposition of the oxychloride produced by heating tungstic acid and carbon in a current of chlorine. (*Annal. de Chim. et de Phys.*, (3,) *50*, 1857, 10.)

J. Dumas: *184* (O = 16).

Dumas made six experiments on the reduction of tungstic acid in hydrogen at a high temperature in a nacelle of unglazed porcelain, and two experiments on the titration of the chloride with argentic nitrate. The extreme difference between the results was 0.69 for O = 8. The acid was pre-

pared by gently heating the ammonium salt in a muffle. (*Annal. de Chim. et de Phys.*, (3,) *55*, 1859, 144.)

F. A. BERNOULLI: 186.8 (O = 16); 1167.5 (O = 100).

Bernoulli made five experiments on the reduction of tungstic acid by hydrogen in a porcelain tube at a very high temperature, two experiments on the amount of water formed in reduction, and four experiments on the oxidation of tungsten. The mean result was W = 93.41; extreme difference, 0.75. [If experiment 9, in which oxidation seems to have taken place, is left out, the mean becomes 93.35; extreme difference, 0.18.] The tungstic acid was prepared from ammonium tungstate which had been boiled for several days with nitric acid. The tungstic acid was heated to redness. One part of it was green, another part yellow. The determinations from the different colored acids did not differ, and Bernoulli considers them isomeric modifications of the same compound. There appear to be misprints in the data given. (*Poggend. Ann.*, *111*, 1860, 599.)

C. SCHEIBLER: 184 (O = 16).

Scheibler reached this value by five determinations of the water contents (9 molecules) of barium metatungstate. From determinations of the barium and the tungsten in the same compound Scheibler reached other values, but he regards the water determination as the most trustworthy. (*Erdmann's Journ. für Prak. Chem.*, *83*, 1861, 328.)

E. ZETTNOW: 183.952 (O = 16).

Determined from analyses of ferrous tungstate and argentic tungstate. A known weight of ferrous tungstate was melted with sodium carbonate and the mass dissolved. The ferric hydrate was thoroughly washed, dissolved in chlorhydric acid, reduced to ferrous chloride with zinc of known composition, and titrated with potassic permanganate in several measured portions. Four such series of experiments were made, and gave a mean of 92.038 for W; extreme difference, 0.33. The ferrous tungstate was prepared by melting pure anhydrous sodium tungstate with ferrous chloride and sodium chloride, dissolving, separating impurities, crystallizing, washing the crystals with water, chlorhydric acid and sodium carbonate. The argen-

tic tungstate was decomposed with nitric acid and titrated with sodium chloride or decomposed with hot sodium chloride solution, the argentic chloride being weighed. Five experiments gave a mean of 91.915 for W; extreme difference, 0.13. The argentic tungstate was prepared by the precipitation of sodium tungstate with argentic nitrate, thorough washing and drying in yellow light. The permanganate solution was prepared according to Mohr and tested with ammonio-ferrous sulphate. Fe = 28, Ag = 108. (*Poggend. Ann.*, *130*, 1867, 30.)

H. E. Roscoe: 184.04 (O = 16).

Determined by reducing tungstic acid in a current of hydrogen, by reoxidizing the metal, and by reducing the chloride in a current of hydrogen, the chlorhydric acid being condensed and estimated as argentic chloride. In the experiments on the acid, that compound was reduced, and reoxidized three times with almost identical results. The mean of the second and third reductions of the same sample gave W = 183.84. In the experiments on the chloride, the chlorine and the tungsten were each determined, and gave a mean of 184.25 for Cl = 35.5. The tungstic acid was prepared by the decomposition of the chloride, washing and heating to redness in a platinum vessel. It was canary yellow. The chloride was prepared from pure tungsten. (*Liebig's Ann.*, *162*, 1872, 366.)

URANIUM.

No certainty exists as to the relation between the equivalent and the atomic weight of uranium. The latter is commonly accepted as about 120. Mendelejeff gives grounds for supposing it to be 240, (*Liebig's Ann.*, *S. 8*, 1871, 178,) and L. Meyer regards it as probably 180, a value which accords well with the specific heat of the black oxide as observed by Regnault. (*Gmelin-Kraut*, *l. c.*) For the purposes of this paper it seems best to retain the customary value.

J. A. Arfvedson: *128.6* (O = 16).

Determined by experiments on the reduction of uranoso-

uranic oxide and on the oxidation of uranous oxide. By combustion of uranous oxide in oxygen he found in two experiments that 100 oxide combined with 3.695 and with 3.73 oxygen. From the reduction of the green oxide he found that 100 uranous oxide combine with 3.67 oxygen. He deduces as the mean 3.688. Regarding uranous oxide as the metal, Arfvedson calculated the atomic weight at 2711.36. [If the lower oxide is a protoxide, the data give 128.6 for O = 16.] The uranous oxide was prepared from pitchblende by solution in aqua regia, precipitation of heavy metals with hydrogen sulphide, precipitation with ammonic hydrate, solution in ammonium carbonate to remove iron, reprecipitation, heating to redness, washing with chlorydric acid to remove impurities, and reduction in hydrogen. (*Poggend. Ann.*, *1*, 1824, 254.)

E. PELIGOT: *119.128* (O = 16).

In two experiments the amount of carbon in the acetate was found to be 11.27 and 11.3; mean 11.285. In one experiment the uranic oxide was determined at 67.3 per cent. [From these data the above value follows.] Peligot takes 120 or 750, C = 75. The preparation of the salt is not given. Peligot mentions the oxalate and gives analyses, but does not deduce an atomic weight from them. (*Annal. de Chim. et de Phys.*, (3,) *5*, 1842, 39.)

J. J. EBELMEN: *118.86* (O = 16); 742.875 (O = 100).

Ebelmen made six experiments on the reduction of the oxalate to uranous oxide by hydrogen and heat. The value follows with an extreme difference of 0.65 for C = 75; H = 12.5. All the weighings were reduced to vacuum. To obtain pure oxalate, the nitrate was precipitated by oxalic acid and this preparation decomposed by heat. The oxide thus obtained was digested with chlorhydric acid, washed, dissolved in nitric acid, recrystallized, and precipitated with oxalic acid. The oxalate was dried at 100°. According to Rammelsberg the reduction of the oxalate is accompanied by the separation of carbon which remains with the oxide. (*Annal. de Chim. et de Phys.*, (3,) *5*, 1842, 189.)

BERZELIUS, ARFVEDSON, MARCHAND: 128.4 (O = 16); 802.49 (O = 100).

While Arfvedson was making his first determination, Berzelius also made an experiment on the combustion of ura-

nous oxide getting 103.685 uranic from 100 uranous oxide. Marchand (*Erdmann's Journ. für Prak. Chem.*, *23*, 1841, 498) got in the same way 103.668. The average of the combustion experiments of all three chemists is 103.694, whence Berzelius calculates the value. (*Berzelius' Jahresbericht*, *22*, 1842, 113.) Peligot and Rammelsberg, as well as Marchand, point out faults in this method, such as the probable condensation of hydrogen in the protoxide and the tendency to form higher oxides. (*Poggend. Ann.*, *59*, 1843, 4.)

C. RAMMELSBERG.

This chemist made experiments on the reduction by hydrogen of the green oxide, prepared in various ways, and got results varying from 580.4 to 767.6 for O = 100. (*Poggend. Ann.*, *59*, 1843, 9.) By precipitation of uranous chloride with silver he reached the number 787.5 for Cl = 442.65. The chlorine contents found varies in three experiments from 73.89 to 74.46. The chloride was prepared by heating uranous oxide in an atmosphere of chlorine. (*Poggend. Ann.*, *55*, 1842, 321.)

J. WERTHEIM: *119.42* (O = 16); 746.36 (O = 100).

Determined by three experiments on the decomposition of the double acetate of uranium and sodium. The mean loss of acetic acid by heating the salt to redness was 32.477 per cent.; extreme difference, 0.036. The number follows for C = 75, H = 6.25, Na = 390.9. [In *Poggend. Ann.*, *57*, 484, an abstract is given of a paper read before the academy (of Berlin?) by Mitscherlich, in which he states that Wertheim's experiments above described give 740.512. Berzelius in his *Jahresbericht*, *23*, 137, makes or quotes the same statement, so also does Rammelsberg, *Poggend. Ann.*, *59*, 4, and it has been repeated elsewhere. I have recalculated the data given by Wertheim and find the results correctly deduced in his own report. For Na = 23.043 (Stas); the data give U = 119.53.] The salt was prepared from uraninite by solution in nitric acid, precipitation with hydrogen sulphide, evaporation of the filtrate to dryness, solution in hot water, crystallization and recrystallization, heating the crystals to drive off nitric acid, solution in acetic acid, digestion with sodium carbonate and recrystallization. (*Erdmann's Journ. für Prak. Chem.*, *29*, 1843, 209.)

C. RAMMELSBERG : about 120 (O = 16).

Determined in six experiments, undertaken at Berzelius' suggestion, by treating uranous oxide with nitric acid and sulphuric acid and weighing the sulphate. It is very difficult to weigh the uranous oxide which constantly increases in weight. Two experiments were made on the green oxide, which was prepared either by heating uranous oxide, or the nitrate, in air. Two experiments were made on magnesium uraniate by dissolving the compound in nitric acid and heating to redness. The compound was found unstable in character. One experiment was made by heating the double acetate of uranium and sodium and three experiments by heating the double acetate of barium and uranium. The results obtained varied from 633.17 to 753.76. Rammelsberg considers the determinations confirmatory of Wertheim's and Ebelmen's. (*Poggend. Ann.*, *66*, 1845, 95.)

E. PELIGOT : 120 (O = 16); 750 (O = 100).

Determined by combustion of the oxalate in a current of air, both the carbonic acid and the green oxide of uranium being weighed. At first Peligot got only 730 as the atomic weight by this process, but by repeating the recrystallization of the salt until determinations gave constant results, he got a mean of 750. He says that he came to the same value by comparing the amount of uranic oxide obtained from the acetate with the weight of the salt employed. (*Paris Comptes Rend.*, *22*, 1846, 487.)

VANADIUM.

Roscoe has determined the vapor density of vanadium chloride. It agrees with an atomic weight of about 51. (*L. Meyer*, *l. c.*)

J. J. BERZELIUS : *52.47* (O = 16).

Berzelius made four experiments on the relation between the higher and the lower oxides of vanadium, three by reduction with hydrogen at a very high temperature and one by oxidation. He supposed the higher oxide to have the formula VO_3, and the lower VO, and consequently got for

the atomic weight the number 855.84 (O = 100). R. Schneider has shown that the data as given by Berzelius are discordant, (*Poggend. Ann.*, *88*, 319,) a fact of small importance in view of the succeeding investigation. The higher oxide analyzed by Berzelius was produced by gently heating the ammonium salt. (*Poggend. Ann.*, *22*, 1831, 14; *Kongl. Vet. Akad. Handl.*, 1831.)

Roscoe examined some ammonium vanadate which Berzelius had sent Faraday and found that it contained phosphorus. (*Liebig's Ann.*, *S*, *6*, 1868, 93.)

H. E. Roscoe: 51.33 (O = 16).

Roscoe made four experiments on the reduction of vanadic acid ($V_2 O_5$) in carefully purified hydrogen. The acid was prepared from ammonium vanadate. To free this compound from phosphorus and silicic acid it was powdered, decrepitated with sodium in an iron crucible, washed with water and with chlorhydric acid, re-oxidized with nitric acid, chloridized in a current of chlorine, the chloride rectified and decomposed with water. The acid so obtained was dried, moistened with sulphuric acid, exposed to the fumes of fluohydric acid for ten days and melted. This pure acid was first heated for several hours in dry air and afterwards in hydrogen. The mean result of four experiments was V = 51.371; extreme difference, 0.228. Nine experiments were made on the titration of the chloride by Pelouze's method. Eight experiments were also made on the analysis of the chloride with argentic nitrate by the ordinary method. The mean of the seventeen experiments on the chloride gives the contents in chlorine at 61.276 per cent.; extreme difference, 0.69. This composition indicates an atomic weight of 51.29. Roscoe takes Cl = 35.457, Ag = 107.93. The vanadium chloride was purified by rectification over sodium in a current of carbon di-oxide. The reagents were prepared according to Stas. (*Liebig's Ann.*, *S*, *6*, 1868, 86.)

Roscoe mentions atomic weight determinations by Czudnowicz as giving 55.35. This chemist, however, did not calculate an atomic weight from his analyses, but used that obtained by Berzelius. (*Poggend. Ann.*, *120*, 1863, 17.)

YTTRIUM.

The composition of yttrium oxide is not definitely settled. Mendelejeff concludes from the general behavior of its compounds that it is a sesqui-oxide. As, however, all the chemists who have made atomic weight determinations of this element have considered it a prot-oxide, I shall assume it to be so and the atomic weight, therefore, about 60.

J. J. Berzelius: *64.29* (O = 16); 401.84 (O = 100).

This determination was made before the discovery of erbium and can scarcely be correct. The value was reached by analysis of the sulphate with barium chloride. Ba = 856.88, S = 201.165. (*Poggend. Ann.*, *8*, 1826, 186; *10*, 1827, 341.)

N. J. Berlin: 59.7 (O = 16).

According to Blomstrand in *Berlin*, *Ber. der Chem. Ges.*, 1873, 1467. I can find no other record of this determination which probably appeared in the *Forhandl. ved de Skandinaviske Naturforsk*, 1860, 448.

O. Popp: 68 (O = 16),

The mean of four analyses of the sulphate showed that 40.15 oxide were equivalent to 38.23 sulphuric anhydride, giving a molecular weight for the oxide of 42.015; extreme difference, 0.013. The yttrium was precipitated with sublimed oxalic acid, the free acid being afterwards neutralized with ammonia. The sulphuric acid was precipitated with barium chloride in the filtrate with precautions. Popp, who denies the existence of erbium and terbium, separated yttrium from the cerite oxides by precipitation with barium carbonate, yttrium remaining in solution, S = 16, Ba = 68.5. (*Liebig's Ann.*, *131*, 1864, 183.)

M. Delafontaine: about 64 (O = 16).

Delafontaine does not pretend that this number is exact. It is derived from analyses of the sulphate. His method of separation was essentially Mosander's, which was proved by Popp and by Bunsen and Bahr to give impure salts. (*Liebig's Ann.*, *134*, 1865, 108.)

BAHR AND BUNSEN: 61.7 (O = 16).

Determined by saturating the oxide with sulphuric acid as in the determination of erbium, *q. v.* Partial recrystallization does not produce pure yttrium nitrate, but only concentrates traces of didymium in the salt. Didymium must be separated with potassic sulphate. Erbium nitrate is more easily decomposed by heat than yttrium nitrate. The nitrates were therefore partially decomposed, yttrium nitrate dissolved out and the process repeated until there was no trace of erbium or didymium visible in the spectroscope. The mean of two determinations gave Y = 30.85; difference, 0.1. S = 16. (*Liebig's Ann.*, *137*, 1866, 21.)

M. DELAFONTAINE: 58.5 (O = 16).

Determined by three experiments on the sulphate which gave in mean 48.23 per cent. oxide for S = 32. [In the *Jahresbericht* this determination is reported as giving Y = 74.5. Yttrium is apparently a misprint for yttrium oxide.] The yttrium salt seems to have been prepared according to the method of Bahr and Bunsen. (*Kopp's Jahresbericht*, 1866, 184; *Bibl. Univ., Arch. des Sciences*, (2), *25*, 1866, 112.)

P. T. CLEVE AND O. M. HOEGLUND: 59.7 (O = 16).

Determined by analysis of the sulphate. The oxide was purified by heating the nitrates, etc., according to N. J. Berlin. (Blomstrand, in *Berlin*, *Bericht der Chem. Ges.*, 1873, 1467; *Bihang till Vet. Akad. Handl*, 1873, B. 1, *3*, No. 8.)

ZINC.

The specific heat of zinc has been determined by Regnault and others. The vapor density of volatile organic compounds has been determined by Frankland and others. These experiments agree in placing the atomic weight at about 65. (*Gmelin-Kraut*, *l. c.*; *L. Meyer*, *l. c.*)

GAY-LUSSAC, BERZELIUS, WOLLASTON: *65.547* (O = 16); *409.67* (O = 100).

In his experiments on the oxidation of zinc Gay-Lussac

found that 100 Zn = 24.41 oxygen. This value is repeatedly cited in his memoir. (*Gilbert's Ann.*, *30*, 1811, 297; *Mémoire D'Arceuil*, *2*, 174.) Wollaston gives the same figures on Gay-Lussac's authority. (*Phil. Trans.*, *104*, 1814, 21.) Wollaston calculates from these data Zn = 410, (O = 100.) Berzelius in each of two experiments got 100 Zn = 124.4 oxide. (*Gilbert's Ann.*, *37*, 1811, 460.) In *Poggend. Ann.*, *8*, 1826, 184, as well as in his *Lehrbuch*, Berzelius cites Gay-Lussac as having found 100 Zn = 24.8 oxygen. He states that his own determinations were in perfect accordance with these figures, and calculates from them the atomic weight of zinc at 403.226 or *64.52*, and this was the accepted value for many years. I cannot find any other determinations by either of these chemists, and am obliged to suppose that there was a mistake made in recording the data from which Berzelius made his calculations; if so, it is remarkable that neither Berzelius nor the other chemists who determined this value perceived it; for the question was reopened during Berzelius' life, and A. Erdmann made his determination at Berzelius' request.

V. A. Jacquelin: *66.24* (O = 16); 414 (O = 100).

This number was reached by measuring the amount of hydrogen developed by a known weight of zinc from sulphuric acid on the supposition that the specific gravity of hydrogen is 0.0624. The results seem to have been inconsistent. Subsequently Jacquelain arrived at the same number by oxidizing an impure zinc of known composition. (*Paris Comptes Rend.*, *14*, 1842, 636; and *Annal. de Chim. et de Phys.*, (3,) *7*, 1843, 204.)

P. A. Favre: *66*, (O = 16); 412.5 (O = 100).

Favre made four experiments on the combustion of zinc oxalate, the carbon di-oxide being collected and its weight compared with that of the oxide. The mean result was Zn = 412.66; extreme difference, 1.11. C = 75. He also made three experiments by passing the hydrogen developed by a known weight of zinc over cupric oxide, the water being caught. These experiments gave in mean Zn = 412.16; extreme difference, 0.65 for H = 12.5. (*Annal. de Chim. et de Phys.*, (3), *10*, 1844, 163.)

A. Erdmann; *65.05* (O = 16); 406.591 (O = 100).

Determined by oxidizing pure zinc with nitric acid, and

driving off the acid by heating the salt in a porcelain crucible. Platinum is attacked. The number is the mean of four experiments; extreme difference, 0.698. The zinc was prepared by mixing pure oxide with carbon, and distilling in a current of hydrogen. (*Berzelius' Jahresbericht*, *24*, 1844, 132; *Œfversigt af Kongl. Vet. Akad. Handl.*, *1*, 3.)

ZIRCONIUM.

Deville and Troost have determined the vapor density of the chloride. It agrees with an atomic weight of about 90. (*L. Meyer*, *l. c.*)

J. J. Berzelius: *89.6* (O = 16).

In one experiment the sulphate was decomposed with ammonic hydrate, the oxide weighed and the sulphuric acid precipitated with barium chloride. In five experiments the sulphate was decomposed at a white heat, ammonium carbonate being added at the close of the operation. The mean result was that 100 parts of sulphuric anhydride unite with 75.853 parts of zirconium oxide; extreme difference, 0.23. Berzelius deduces the value 840.08 for O = 100, S = 201.165; on the supposition that the oxide contains three atoms of oxygen. [Being a binoxide, this relation gives Zr = 89.6 for O = 16.] The sulphate seems to have been prepared by dissolving the oxide in sulphuric acid and expelling the excess of acid by heat. (*Poggend. Ann.*, *4*, 1825, 126.)

R. Hermann:

This chemist made some experiments on the chloride getting in three determinations a mean of 839.45 for O = 100 and on the tri-oxide supposition. The extreme difference was 20.1. Cl = 443.65. The chloride was produced by heating the oxide with carbon in a current of chlorine. Hermann adopts not his own but Berzelius' determination. (*Erdmann's Journ. für Prak. Chem.*, *31*, 1844, 77.)

C. Marignac: 90 (O = 16).

Determined from analyses of potassium fluo-zirconiate. The salt was decomposed with sulphuric acid, the excess

of acid driven off by heat, the residue weighed, the potassic sulphate leached out with water, and the residue again weighed. Marignac does not pretend that the determination is accurate. The results gave from 45.01 to 45.48. He thinks that some potassic sulphate may have escaped solution, and therefore takes the minimum. K = 39, S = 16.

According to Marignac, Deville also found the atomic weight of zirconium somewhat higher than Berzelius by analysis of the chloride with which he determined the vapor density. (*Annal. de Chim. et de Phys.*, (3,) *60*, 1860, 257.)

APPENDIX.

DETERMINATIONS BY T. THOMSON.

In *Thomson's Annals of Philosophy*, volumes *16* and *17*, 1820-21, Thomson published a series of papers descriptive of experiments undertaken for the purpose of verifying Prout's hypothesis. His method consisted in mixing re-agents in what he considered equivalent proportions, and after precipitation examining portions of the supernatant liquid for an excess of each of the salts supposed to neutralize one another. In all except four cases, either the salt analyzed was a sulphate and the precipitant barium chloride, or the determination was dependent upon such an analysis; yet although Thomson took barium = 70, in no instance was he able to detect either barium or sulphuric acid in the residual solution when the quantity of the re-agents corresponded to the atomic weights which he adopts. Comparison of his results with those reached by more accurate experimenters will make this exact neutralization appear impossible, nor were his contemporaries able to repeat his experiments successfully. Thomson's determinations are, as such, utterly valueless, yet as they were for many years extensively accepted in English and American scientific literature they are inserted here for reference. In the following table Thomson's numbers are multiplied, when necessary, for the sake of comparison with the values now accepted.

DETERMINATIONS INVOLVING BARIUM = 70.

Arsenic	76	Magnesium	24
Barium	140	Manganese	56
Bismuth	216	Nickel	52
Calcium	40	Nitrogen	14
Carbon	12	Phosphorus	32
Chlorine	36	Potassium	40
Chromium	56	Silver	110
Cobalt	52	Sodium	24
Copper	64	Strontium	88
Iron	56	Sulphur	32
Lead	208	Zinc	68

THOMSON FURTHER DETERMINED—

Antimony at	132	by oxidation.
Boron at	12	from analysis of borax.
Mercury at	200	by conversion of the oxide into chloride.
Tin at	116	by oxidation with nitric acid.

REDUCTION OF WEIGHINGS TO VACUUM.

In discussing the analyses recorded in the foregoing pages, or in reconciling atomic weight determinations by various chemists, it may be found convenient to employ the following table. The maximum error involved is less than 0.01 per cent. or 0.1 milligram per gram.

GRAM WEIGHTS BEING OF BRASS, FRACTIONS OF PLATINUM.

For substances the sp. gr. of which exceeds 6.1; no correction is necessary.

For substances the sp. gr. of which is less than 6.1:—

To correct the entire grams; multiply their number by the correction in the table opposite the sp. gr. of the substance, found in the *first* column, and add the product to the observed weight.

To correct the fractions of a gram, multiply the correction opposite the sp. gr. of the substance, found in the *third* column of the table, by the first two decimal figures of the observed weight, if the sp. gr. of the substance is *less* than 3, and by the first decimal only, if the sp. gr. exceeds 3, and add the product to the observed weight.

ALL WEIGHTS USED BEING OF PLATINUM.

For substances the sp. gr. of which exceeds 7.8, no correction is necessary.

For substances the sp. gr. of which is less than 7.8:—Multiply the correction opposite the sp. gr. of the substance, found in the *third* column, by the number of grams, tenths and hundredths observed, if the sp. gr. falls short of 3, or by the number of grams and tenths, if the sp. gr. exceeds 3, and add the product to the observed weight.

The table shows within what limits it is necessary to know the sp. gr.

(Weights of Brass) for Specific Gravity between—		Correction per Gram. Error $< \frac{1}{30}$ Mg.	(Weights of Platinum) for Specific Gravity between—	
27.738 and	11.064	—0.000 067 gram.		
11.064	6.904	0.000 000	51.766 and	13.568
6.904	5.019	+0.000 067	13.568	7.807
5.019	3.943	0.000 133	7.807	5.480
3.943	3.247	0 000 200	5.480	4.222
3.247	2.759	0.000 267	4.222	3.433
2.759	2.399	0 000 333	3.433	2.893
2.399	2.122	0.000 400	2.893	2.500
2.122	1.903	0.000 467	2.500	2.201
1.903	1.724	0.000 533	2.201	1.965
1.724	1.576	0.000 600	1.965	1.776
1.576	1.452	0.000 667	1.776	1.619
1.452	1.377	0.000 733	1.619	1.488
1.377	1.254	0 000 800	1.488	1.377
1.254	1.174	0.000 867	1.377	1.281
1.174	1.103	0.000 933	1.281	1.197
1.103	1.041	0.001 000	1.197	1.124
1.041	0.985	0.001 067	1.124	1.059
		0.001 133	1.059	1.002
		0.001 200	1.002	0.950

(*Sill. Amer. Jour.*, *16*, 1878, 265; *Liebig's Ann.*, *195*, 1879, 222.)

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SMITHSONIAN MISCELLANEOUS COLLECTIONS.

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THE CONSTANTS OF NATURE.

PART V.

A RECALCULATION

—OF—

THE ATOMIC WEIGHTS.

BY

FRANK WIGGLESWORTH CLARKE, S. B.,

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WASHINGTON:

SMITHSONIAN INSTITUTION.

1882.

ADVERTISEMENT.

The present publication is one of a series devoted to the discussion and more precise determination of various "Constants of Nature;" and forms the *Fifth* contribution to that subject published by this Institution.

The *First* number of the series, embracing tables of "Specific Gravities" and of Melting and Boiling Points of Bodies, prepared by the same author, Prof. F. W. Clarke, was published in 1873. The *Fourth* part of the series, comprising a complete digest of the various "Atomic Weight" determinations of the chemical elements published since 1814, commencing with the well-known "Table of Equivalents" by Wollaston, (given in the Philosophical Transactions for that year,) compiled by Mr. George F. Becker, was published by the Institution in 1880. The present work which may be regarded as practically supplementary to that digest, (or perhaps rather as the memoir to which that digest is introductory,) comprises a very full discussion and re-calculation of the "Atomic Weights" from all the existing data, and the assignment of the most probable value to each of the elements.

The manuscript of the work was presented to the Institution in its completed form by Prof. F. W. Clarke, the cost of publication only being at the expense of the Smithsonian fund.

SPENCER F. BAIRD,
Secretary of Smithsonian Institution.

WASHINGTON, *January*, 1882.

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INTRODUCTION.

In the autumn of 1877 the writer began collecting data relative to the determinations of atomic weights, with the purpose of preparing a complete resumé of the entire subject, and of recalculating all the estimations. The work was fairly under way, the material was collected and partly discussed, when I received from the Smithsonian Institution a manuscript by Professor George F. Becker, entitled "Atomic Weight Determinations: a Digest of the Investigations Published since 1814." This manuscript, which has lately been issued as Part IV of the "Constants of Nature," covered much of the ground contemplated in my own undertaking. It brought together all the evidence, presenting it clearly and thoroughly in compact form; in short, that portion of the task could not well be improved upon. Accordingly, I decided to limit my own labors to a critical recalculation of the data; to combine all the figures upon a common mathematical basis, and to omit everything which could as well be found in Professor Becker's "Digest."

At the very beginning of my work certain questions confronted me. Should I treat the investigations of different individuals separately, or should I combine similar data together in a manner irrespective of persons? For example, ought I, in estimating the atomic weight of silver, to take Stas' work by itself, Marignac's work by itself, and so on, and then average the results together; or should I rather combine all series of figures relating to the composition of potassium chlorate into one mean value, and all the data concerning the composition of silver chloride into another mean, and, finally, compute from such general means the constant sought to be established? The latter plan was finally adopted; in fact, it was rendered necessary by the method of least squares, which method was alone adequate to supply me with good processes for calculation.

The mode of discussion and combination of results was briefly as follows. The formulæ employed are given in another chapter. I began with the ratio between oxygen and hydrogen; in other words, with the atomic weight of oxygen referred to hydrogen as unity. Each series of experiments was taken by itself, its arithmetical mean was found, and the probable error of that mean was computed. Then the several means were combined according to the appropriate formula, each receiving a weight dependent upon its probable error. The general mean thus established was taken as the most probable value for the atomic weight of oxygen, and, at the same time, its probable error was mathematically asssigned.

Next in order came a group of elements which were best discussed together, namely, silver, chlorine, potassium, sodium, bromine, iodine, and sulphur. For these elements there were data from thirteen experimenters. All similar figures were first reduced to common standards, and then the means of individual series were combined into general means. Thus all the data were condensed into twenty ratios, from which several independent values for the atomic weight of each element could be computed. The probable errors of these values, however, all involved the probable error of the atomic weight of oxygen, and were, therefore, higher than they would have been had the latter element not entered into consideration. Here, then, we have suggested a chief peculiarity of this whole revision. The atomic weight of each element involves the probable errors of all the other elements to which it is directly or indirectly referred. Accordingly, an atomic weight determined by reference to elements whose atomic weights have been defectively ascertained will receive a high probable error, and its weight, when combined with other values, will be relatively low. For example, an atomic weight ascertained by direct comparison with hydrogen will, other things being equal, have a lower probable error than one which is referred to hydrogen through the intervention of oxygen; and a metal whose equivalent involves only the probable error of oxygen

will be more exactly known than one which depends upon the greater errors of silver and chlorine. These points will appear more clearly evident in the subsequent actual discussions.

But although the discussion of atomic weights is ostensibly mathematical, it cannot be purely so. Chemical considerations are necessarily involved at every turn. In assigning weights to mean values I have been, for the most part, rigidly guided by mathematical rules; but in some cases I have been compelled to reject altogether series of data which were mathematically excellent, but chemically worthless because of constant errors. In certain instances there were grave doubts as to whether particular figures should be included or rejected in the calculation of means; there having been legitimate reasons for either procedure. Probably many chemists would differ with me upon such points of judgment. In fact, it is doubtful whether any two chemists, working independently, would handle all the data in precisely the same way, or combine them so as to produce exactly the same final results. Neither would any two mathematicians follow identical rules or reach identical conclusions. In calculating the atomic weight of any element those values are assigned to other elements which have been determined in previous chapters. Hence a variation in the order of discussion might lead to slight differences in the final results.

As a matter of course the data herein combined are of very unequal value. In many series of experiments the weighings have been reduced to a vacuum standard; but in most cases chemists have neglected this correction altogether. In a majority of instances the errors thus introduced are slight; nevertheless they exist, and interfere more or less with all attempts at a theoretical consideration of the results. For example, they affect seriously the investigation of Prout's hypothesis, and are often great enough to account for seeming exceptions to it. Such questions as these will be considered in the appendix.

Another serious source of error affecting many of the re-

sults was not discovered until recently. A large number of computations had been actually finished, involving, among other things, the greater part of Stas' work, when Dumas published his investigation upon the occlusion of oxygen by silver. Here it was shown that a very great number of atomic weight determinations must have been vitiated by constant errors, which, though constant for each series, were probably of different magnitude in different series, and, therefore, could not be systematically corrected for. At the time of the announcement of this discovery of Dumas my work was so far under way that I thought it best to complete my discussion without reference to it, and then to study its influence in the appendix. In the chapter upon aluminum, however, it will be noted that Mallet eliminated this error in great part from his experimental results.

Necessarily, this work omits many details relative to experimental methods, and particulars as to the arrangements of special forms of apparatus. For such details original memoirs must be consulted. Their inclusion here would have rendered the work unwarrantably bulky. There is such a thing as over-exhaustiveness of treatment, which is equally objectionable with under-thoroughness.

Of course, none of the results reached in this revision can be considered as final. Every one of them is liable to repeated corrections. To my mind the real value of the work, great or little, lies in another direction. The data have been brought together and reduced to common standards, and for each series of figures the probable error has been determined. Thus far, however much my methods of combination may be criticized, I feel that my labors will have been useful. The ground is now cleared, in a measure, for future experimenters; it is possible to see more distinctly what remains to be done; some clues are furnished as to the relative merits of different series of results. I hope to be able, from time to time, as new determinations are published, to continue the task here begun, and perhaps, also, to add, in the near future, some data of my own establishing.

In addition to the usual periodicals the following works

have been freely used by me in the preparation of this volume:

BERZELIUS, J. J. Lehrbuch der Chemie. 5 Auflage. Dritter Band. SS. 1147–1231. 1845.

VAN GEUNS, W. A. J. Prœve eener Geschiedenis van de Æquivalentgetallen der Scheikundige Grondstoffen en van hare Soortelijke Gewigten in Gasvorm, voornamelijk in Betrekking tot de vier Grondstoffen der Bewerktuigde Natuur. Amsterdam, 1853.

MULDER, E. Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 13 Eenvoudige Ligchamen. Utrecht, 1853.

MULDER, L. Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 24 Metalen. Utrecht, 1853.

OUDEMANS, A. C., Jr. Historisch-Kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van Twee en Twintig Metalen. Leiden, 1853.

STAS, J. S. Untersuchungen über die Gesetze der Chemischen Proportionen über die Atomgewichte und ihre gegenseitigen Verhältnisse. Uebersetzt von Dr. L. Aronstein. Leipzig, 1867.

The four Dutch monographs above cited are especially valuable. They represent a revision of all atomic weight data down to 1853, as divided between four writers.

FORMULÆ FOR THE CALCULATION OF PROBABLE ERROR.

Although the ordinary formula for the probable error of an arithmetical mean is familiar to all physicists, it is perhaps best to reproduce it here, as follows:

(1.) $$e = \pm .6745 \sqrt{\frac{S}{n(n-1)}}$$

Here n represents the number of observations or experiments in the series, while S is the sum of the variations of the individual results from the mean.

In combining several arithmetical means, representing several series, into one general mean each receives a weight indicated by its probable error; greater as the latter becomes less, and *vice versa*. Let A, B, C, etc., be such mean results, and a, b, c, their probable errors respectively. Then the general mean is determined by this formula:

(2.) $$M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \ldots}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \ldots}$$

For the probable error of this general mean we have:

(3.) $$m = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \ldots}}$$

In the calculation of atomic and molecular weights the following formulæ have been employed. For assistance in connection with them my thanks are due to Professors H. T. Eddy and E. W. Hyde of the University of Cincinnati.

Using, as before, capital letters to represent known quantities and small letters for their probable errors respectively,

we have for the sum or difference of two quantities, A and B:

(4.) $$e = \sqrt{a^2 + b^2}$$

For the product of A multiplied by B the probable error is

(5.) $$e = \sqrt{(Ab)^2 + (Ba)^2}$$

For the product of three quantities, ABC:

(6.) $$e = \sqrt{(BCa)^2 + (ACb)^2 + (ABc)^2}$$

For a quotient, $\frac{B}{A}$, the probable error becomes

(7.) $$e = \frac{\sqrt{\left(\frac{Ba}{A}\right)^2 + b^2}}{A}$$

Given a proportion, A : B : : C : x, the probable error of the fourth term is as follows:

(8.) $$e = \frac{\sqrt{\left(\frac{BCa}{A}\right)^2 + (Cb)^2 + (Bc)^2}}{A}.$$

This formula is used in nearly every atomic weight calculation, and is, therefore, exceptionally important. Rarely a more complicated case arises in a proportion of this kind:

$$A : B : : C + x : D + x$$

In this proportion the unknown quantity occurs in two terms. Its probable error is found by this expression, and is always large:

(9.) $$e = \sqrt{\frac{(C-D)^2}{(A-B)^4}(B^2a^2 + A^2b^2) + \frac{B^2c^2 + A^2d^2}{(A-B)^2}}$$

When several independent values have been calculated for an atomic weight they are treated like means, and combined according to formulæ (2) and (3.) Each final result

is, therefore, to be regarded as the general mean of all reliable determinations. This method of combination may not be the best one theoretically possible, but it seemed to be the only one practically available. The data are too imperfect to warrant the use of much more elaborate processes of discussion.

RECALCULATION OF THE ATOMIC WEIGHTS.

OXYGEN.

The ratio between oxygen and hydrogen is the foundation upon which the entire system of atomic weights depends. Hence, the accuracy of its determination has, from the beginning, been recognized as of extreme importance. A trifling error here may become cumulative when repeated through a moderate series of other ratios.

Leaving out of account the earliest researches, which have now only a historical value, we find that three methods have been employed for fixing this important constant. First, the synthesis of water, effected by passing hydrogen gas over red hot oxide of copper. Secondly, the exact determination of the relative density of the two gases. Thirdly, by weighing the quantity of water formed upon the direct union of a known volume of hydrogen with oxygen.

The first of these methods has been employed in three leading investigations, namely, by Dulong and Berzelius,* by Dumas, and by Erdmann and Marchand. The essential features of the method are in all cases the same. Hydrogen gas is passed over heated oxide of copper, and the water thus formed is collected and weighed. From this weight and the loss of weight which the oxide undergoes, the exact composition of water is readily calculated. Dulong and Berzelius made but three experiments, with the following results for the percentages of oxygen and hydrogen in in water:

O.	H.
88.942	11.058
88.809	11.191
88.954	11.046

* Thomson's Annals of Philosophy, July, 1821, p. 50.

These figures, rather roughly determined, and by no means exact enough to meet the requirements of modern science, give a mean value of 16.021 for the atomic weight of oxygen. As the weighings were not reduced to a vacuum, this correction was afterwards applied by Clark,* who showed that these syntheses really make O = 15.894; or, in Berzelian terms, if O = 100, H = 12.583.

In 1842 Dumas† published his elaborate investigation upon the composition of water. The first point was to get pure hydrogen. This gas, evolved from zinc and sulphuric acid, might contain oxides of nitrogen, sulphur dioxide, hydrosulphuric acid, and arsenic hydride. These impurities were removed in a series of wash bottles; the H_2S by a solution of lead nitrate, the H_3As by silver sulphate, and the others by caustic potash. Finally, the gas was dried by passing through sulphuric acid, or, in some of the experiments, over phosphorus pentoxide. The copper oxide was thoroughly dried, and the bulb containing it was weighed. By a current of dry hydrogen all the air was expelled from the apparatus, and then, for ten or twelve hours, the oxide of copper was heated to dull redness in a constant stream of the gas. The reduced copper was allowed to cool in an atmosphere of hydrogen. The weighings were made with the bulbs exhausted of air. The following table gives the results:

Column A contains the symbol of the drying substance. B gives the weight of the bulb and copper oxide. C, the weight of bulb and reduced copper. D, the weight of the vessel used for collecting the water. E, the same, plus the water. F, the weight of oxygen. G, the weight of water formed. H, the crude equivalent of H when O = 10,000. I, the equivalent of H, corrected for the air contained in the sulphuric acid employed. This correction is not explained, and seems to be questionable.

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* Philosophical Magazine, 3d series, 20, 341.

† Compt. Rend., 14, 537.

A.	B.	C.	D.	E.	F.	G.	H.	I.
H_2SO_4	291.985	278.806	480.807	495.634	13.179	14.827	1250.5	1249.6
"	344.548	324.186	488.227	511.132	20.362	22.905	1249.0	1248.0
"	316.671	296.175	439.711	462.764	20.495	23.053	1248.1	1247.2
P_2O_5	625.829	568.825	884.190	948.323	57.004	64.044	1250.6	1249.0
H_2SO_4	804.546	728.182	887.331	973.291	76.364	85.960	1256.2	1254.6
"	533.726	490.155	867.159	916.206	43.571	49.047	1256.3	1255.0
"	661.915	627.104	839.304	878.482	34.811	39.178	1254.6	1253.3
P_2O_5	612.625	566.738	824.624	876.244	45.887	51.623	1250.0	1249.0
"	904.643	844.612	822.660	890.246	60.031	67.586	1258.3	1255.1
H_2SO_4	642.325	590.487	741.095	799.417	51.838	58.320	1250.4	1248.9
P_2O_5	587.645	535.137	874.832	933.910	52.508	59.078	1251.2	1249.0
"	673.280	613.492	931.487	998.700	59.789	67.282	1253.3	1250.8
H_2SO_4	660.855	598.765	682.374	752.273	62.090	69.899	1257.7	1254.8
"	642.325	590.487	741.097	799.455	51.838	58.360	1258.1	1256.2
"	937.845	881.362	1064.762	1128.319	56.483	63.577	1255.8	1252.2
P_2O_5	756.352	719.563	878.640	920.030	36.789	41.390	1250.6	1249.1
"	754.162	720.000	887.817	926.275	34.162	38.458	1257.3	1255.1
"	759.762	727.632	888.662	924.837	32.133	36.175	1257.5	1254.7
"	747.652	716.825	877.862	912.539	30.827	34.677	1248.8	1248.0
						Means	1253.3	1251.5

In the sum total of these nineteen experiments, 840.161 grammes of oxygen form 945.439 grammes of water. This gives, in percentages, for the composition of water, oxygen 88.864; hydrogen, 11.136. Hence the atomic weight of oxygen, calculated in mass, is 15.9608. In the following column the values are given as deduced from the individual data given under the headings F and G:

15.994
16.014
16.024
15.992
15.916
15.916
15.943
16.000
15.892
15.995
15.984
15.958
15.902
15.987
15.926
15.992
15.904
15.900
16.015

Mean, 15.9607, with a probable error of ± .0070.

In calculating the above column several discrepancies were noted, probably due to misprints in the original memoir. On comparing columns B and C with F, or D and E with G, these anomalies chiefly appear. They were detected and carefully considered in the course of my own calculations; and, I believe, eliminated from the final result.

The paper by Erdmann and Marchand* followed closely after that of Dumas. The method of research was essentially the same as that of the latter chemist, varying only in points of comparatively unimportant detail. The results are given in two series, in one of which the weighings were

* Journ. f. Prakt. Chem., 1842, bd. 26, s. 461.

not actually made in vacuo, but were, nevertheless, reduced to a vacuum standard. The second series represents actual vacuum weighings. The quantity of water formed in each experiment, was from 41.664 to 95.612 grammes. I give below only the percentages of oxygen and hydrogen in water as deduced from Erdmann and Marchand's data:

First Series.

O.	H.
88.836	11.164
88.821	11.179
88.874	11.126
88.868	11.132

Second Series.

O.	H.
88.887	11.113
88.898	11.102
88.895	11.105
88.899	11.101

Hence, the atomic weight of oxygen is, as follows:

First Series.	*Second Series.*
15.915	15.997
15.891	16.015
15.976	16.010
15.966	16.016
Mean, 15.9369, ± .0138	Mean, 16.0095, ± .0030

The effect of discussing these two series separately is somewhat startling. It gives to the four experiments in Erdmann and Marchand's second group a weight vastly greater than their other four and Dumas' nineteen taken together. For so great a superiority as this there is no adequate reason; and it is highly probable that it is due almost entirely to fortunate coincidences, rather than to greater accuracy of work. We will, therefore, treat Erdmann and Marchand's experiments as one series, giving all equal weight, and then combine them with the results obtained by Dumas. We now have—

By Dumas	O = 15.9607, ± .0070
By Erdmann and Marchand	O = 15.9733, ± .0113
General mean	O = 15.9642, ± .0060

In discussing the relative density of oxygen and hydrogen gases we need only consider the more modern researches of Dumas and Boussingault, and of Regnault. As the older work has some historical value, I may in passing just cite its results. For the density of hydrogen we have .0769, Lavoisier; .0693, Thomson; .092, Cavendish; .0732, Biot and Arago; .0688, Dulong and Berzelius. For oxygen there are the following determinations: 1.087, Fourcroy, Vauquelin, and Séguin; 1.103, Kirwan; 1.128, Davy; 1.088, Allen and Pepys; 1.1036, Biot and Arago; 1.1117, Thomson; 1.1056, De Saussure; 1.1026, Dulong and Berzelius; 1.106, Buff; 1.1052, Wrede.*

In 1841 Dumas and Boussingault† published their determinations of gaseous densities. For hydrogen they obtained values ranging from .0691 to .0695; but beyond this mere statement they give no details. For oxygen three determinations were made, with the following results:

1.1055
1.1058
1.1057

Mean, 1.10567, ± .00006

If we take the two extreme values given above for hydrogen, and regard them as the entire series, they give us a mean of .0693, ± .00013.

This mean hydrogen value, combined with the mean oxygen value, gives for the atomic weight of the latter element the number 15.9538, ± .031.

Regnault's researches, published four years later,‡ were of

* For Wrede's work, see Berzelius' Jahresbericht for 1843. For Dulong and Berzelius, see the paper already cited. All the other determinations are taken from Gmelin's Handbook, Cavendish edition, v. 1, p. 279.

† Compt. Rend., 12, 1005. Compare also with Dumas, Compt. Rend., 14, 537.

‡ Compt. Rend., 20, 975.

a more satisfactory kind. Indeed, they are among the classics of physical science; and probably approach as near to absolute accuracy as is possible for experiment.

For hydrogen three determinations of density gave the following results:

.06923
.06932
.06924

Mean, .069263, $\pm$ .000019

For oxygen four determinations were made, but in the first one the gas was contaminated by traces of hydrogen, and the value obtained, 1.10525; was, therefore, rejected by Regnault as too low. The other three are as follows:

1.10561
1.10564
1.10565

Mean, 1.105633, $\pm$ .000008

Now, combining the hydrogen and oxygen series, we have for the atomic weight of oxygen, 15.9628, $\pm$ .0044.*

Upon combining the result of Regnault's work with that from Dumas and Boussingault's we get the following value:

From Dumas and Boussingault	O = 15.9538, $\pm$ .031
From Regnault	O = 15.9628, $\pm$ .0044
General mean	O = 15.9627, $\pm$ .0043

This result, it will be seen, agrees remarkably well with that obtained in the experiments upon the synthesis of water.

* Since these computations were made, Professor John Le Conte has called my attention to the existence of slight numerical errors in Regnault's own reductions. As corrected by Le Conte, Regnault's figures give 1.105612 for the density of oxygen, and 0.069269 for that of hydrogen. Hence the atomic weight of O becomes 15.9611, instead of 15.9628. The difference is slight, but still it ought not to be ignored. All the computations in the body of this work, having been finished before I received Professor Le Conte's figures, must stand, nevertheless, as they are. For further details Le Conte refers to Phil. Mag., (4.) 27, p. 29, 1864; and also to the Smithsonian Report for 1878, p. 428.

The third method indicated at the beginning of this discussion has been recently employed in part by J. Thomsen* of Copenhagen. Unfortunately this chemist has not published the details of his work, but only the end results. These serve to confirm the values for oxygen fixed by other methods, but they cannot well be included in the systematic discussion. Partly by the oxidation of hydrogen over heated copper oxide, and partly by its direct union with oxygen, Thomsen finds that at the latitude of Copenhagen, and at sea level, one litre of dry hydrogen at 0° and 760 mm. pressure will form .8041 gramme of water. According to Regnault, at this latitude, level, temperature, and pressure, a litre of hydrogen weighs .08954 gramme. From these data, O = 15.9605. It will be seen at once that Thomsen's work depends in great part upon that of Regnault, and yet that it affords an admirable reinforcement of the latter.

It is now plain, in conclusion, that all the different lines of research point to an atomic weight for oxygen a little below 16.00. Five distinct investigations confirm each other wonderfully. Upon combining the values obtained by the two chief methods we get the following final results:

From synthesis of water	O = 15.9642, ± .0060
From gaseous densities	O = 15.9627, ± .0043

In the general mean the atomic weight of oxygen becomes 15.9633, with a probable error of ± .0035.†

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* Ber. d. Deutsch. Chem. Gesellschaft, 1870, s. 928.

† Le Conte's correction of Regnault's figures introduced here would make O = 15.9622, instead of 15.9633. Difference, .0011.

SILVER, POTASSIUM, SODIUM, CHLORINE, BROMINE, IODINE, AND SULPHUR.

The atomic weights of these seven elements depend upon each other to so great an extent that they can hardly be considered independently. Indeed, chlorine, potassium, and silver have always been mutually determined. From the ratio between silver and chlorine, the ratio between silver and potassium chloride, and the composition of potassium chlorate, these three atomic weights were first accurately fixed. Similar ratios, more recently worked out by Stas and others, have rendered it desirable to include bromine, iodine, sulphur, and sodium in the same general discussion.

Several methods of determination will be left altogether out of account. For example, in 1842 Marignac* sought to fix the atomic weight of chlorine by estimating the quantity of water formed when hydrochloric acid gas is passed over heated oxide of copper. His results were wholly inaccurate, and need no further mention here. A little later Laurent† redetermined the same constant from the analysis of a chlorinated derivative of naphthalene. This method did not admit of extreme accuracy, and it presupposed a knowledge of the atomic weight of carbon; hence it may be properly disregarded. Maumené's‡ analyses of the oxalate and acetate of silver gave good results for the atomic weight of that metal; but they also depend for their value upon our knowledge of carbon, and will, therefore, be discussed further on with reference to that element.

Let us now consider the ratios upon which we must rely for ascertaining the atomic weights of the seven elements in question. After we have properly arranged our data we may then discuss their meaning. First in order we may

* Compt. Rend., 14, 570. Also, Journ. f. Prakt. Chem., 26, 304.
† Compt. Rend., 14, 456. Journ. f. Prakt. Chem., 26, 307.
‡ Ann. d. Chim. et d. Phys., (3,) 18, 41. 1846.

conveniently take up the percentage of potassium chloride obtainable from the chlorate.

The first reliable series of experiments to determine this percentage was made by Berzelius.* All the earlier estimations were vitiated by the fact that when potassium chlorate is ignited under ordinary circumstances a little solid material is mechanically carried away with the oxygen gas. Minute portions of the substance may even be actually volatilized. These sources of loss were avoided by Berzelius, who devised means for collecting and weighing this trace of potassium chloride. All the successors of Berzelius in this work have benefitted by his example; although for the methods by which loss has been prevented we must refer to the original papers of the several investigators. In short, then, Berzelius ignited potassium chlorate, and determined the percentage of chloride which remained. Four experiments gave the following results:

60.854
60.850
60.850
60.851

Mean, 60.851, with a probable error of ± .0006

The next series was made by Penny,† in England, who worked after a somewhat different method. He treated potassium chlorate with strong hydrochloric acid in a weighed flask, evaporated to dryness over a sand bath, and then found the weight of the chloride thus obtained. His results are as follows, in six trials:

60.825
60.822
60.815
60.820
60.823
60.830

Mean, 60.8225, ± .0014

* Poggend. Annalen, 1826, bd. 8, s. 1.
† Phil. Transactions, 1839, p. 20.

In 1842 Pelouze* made three estimations by the ignition of the chlorate, with these results:

60.843
60.857
60.830

Mean, 60.843, ± .0053

Marignac, in 1842,† worked with several different recrystallizations of the commercial chlorate. He ignited the salt, with the usual precautions for collecting the material carried off mechanically, and also examined the gas which was evolved. He found that the oxygen from 50 grammes of chlorate contained chlorine enough to form .003 gramme of silver chloride. Here are the percentages found by Marignac:

In chlorate once crystallized	60.845
In chlorate once crystallized	60.835
In chlorate twice crystallized	60.833
In chlorate twice crystallized	60.844
In chlorate three times crystallized	60.839
In chlorate four times crystallized	60.839
Mean,	60.8392, ± .0013

In the same paper Marignac describes a similar series of experiments made upon potassium perchlorate, $KClO_4$. In three experiments it was found that the salt was not quite free from chlorate, and in three more it contained traces of iron. A single determination upon very pure material gave 46.187 per cent. of oxygen and 53.813 of residue.

In 1845 two series of experiments were published by Gerhardt.‡ The first, made in the usual way, gave these results:

60.871
60.881
60.875

Mean. 60.8757, ± .0020

* Compt. Rend., 15, 959.
† Ann. d. Chem. u. Pharm., bd. 44, s. 18.
‡ Compt. Rend., 21, 1280.

In the second series the oxygen was passed through a weighed tube containing moist cotton, and another filled with pumice stone and sulphuric acid. Particles were thus collected which in the earlier series escaped. From these experiments we get—

60.947
60.947
60.952

Mean, 60.9487, ± .0011

These last results were afterwards sharply criticized by Marignac,* and their value seriously questioned.

The next series, in order of time, is due to Maumené.† This chemist supposed that particles of chlorate, mechanically carried away, might continue to exist as chlorate, undecomposed; and hence that all previous series of experiments might give too high a value to the residual chloride. In his determinations, therefore, the ignition tube, after expulsion of the oxygen, was uniformly heated in all its parts. Here are his percentages of residue:

60.788
60.790
60.793
60.791
60.785
60.795
60.795

Mean, 60.791, ± .0009

The question which most naturally arises in connection with these results is, whether portions of chloride may not have been volatilized, and so lost.

Closely following Maumené's paper there is a short note by Faget,‡ giving certain mean results. According to this chemist, when potassium chlorate is ignited slowly, we get

* Supp. Bibl. Univ. de Genéve, Vol. I.
† Ann. d. Chim. et d. Phys., (3,) 18, 71. 1846.
‡ Ann. d. Chim. et d. Phys., (3,) 18, 80. 1846.

60.847 per cent. of residue. When the ignition is rapid, we get 60.942. As no detailed experiments are given, these figures can have no part in our discussion.

Last of all we have two series determined by Stas.* In the first series we have the results obtained by igniting the chlorate. In the second series the chlorate was reduced by strong hydrochloric acid, after the method followed by Penny:

First Series.

60.8380
60.8395
60.8440
60.8473
60.8450

Mean, 60.84276, ± .0012

Second Series.

60.850
60.853
60.844

Mean, 60.849, ± .0017

In these experiments every conceivable precaution was taken to avoid error and ensure accuracy. All weighings were reduced to a vacuum standard; from 70 to 142 grammes of chlorate were used in each experiment; and the chlorine carried away with the oxygen in the first series was absorbed by finely divided silver and estimated. It is difficult to see how any error could have crept in.

Now, to combine these different series of experiments.

Berzelius,	mean result	60.851,	± .0006
Penny,	"	60.8225,	± .0014
Pelouze,	"	60.843,	± .0053
Marignac,	"	60.8392,	± .0013
Gerhardt, 1st	"	60.8757,	± .0020
" 2d	"	60.9487,	± .0011
Maumené,	"	60.791,	± .0009
Stas, 1st	"	60.8428,	± .0012
" 2d	"	60.849,	± .0017
General mean, from all nine series, representing forty experiments		60.846,	± .00038

* See Aronstein's Translation, p. 249.

This value is exactly that which Stas deduced from both of his own series combined, and gives great emphasis to his wonderfully accurate work. It also finely illustrates the compensation of errors which occurs in combining the figures of different experimenters.

Similar analyses of silver chlorate have been made by Marignac and by Stas. Marignac's figures I have not been able to find,* and Stas gives but two experiments. The following are his percentages of oxygen in silver chlorate:†

25.081
25.078

Mean, 25.0795, ± .0010

For the direct ratio between silver and chlorine there are seven available series of experiments. Here, as in many other ratios, the first reliable work was done by Berzelius.‡

He made three estimations, using each time twenty grammes of pure silver. This was dissolved in nitric acid. In the first experiment the silver chloride was precipitated and collected on a filter. In the second and third experiments the solution was mixed with hydrochloric acid in a flask, evaporated to dryness, and the residue then fused and weighed without transfer. One hundred parts of silver formed of chloride:

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* Since all the calculations were finished I have secured a copy of Marignac's figures. They are as follows: The third column gives the percentage of O in $AgClO_3$.

24.510 grm. $AgClO_3$ gave	18.3616 AgCl.	25.103
25.809 " "	19.3345 "	25.086
30.306 " "	22.7072 "	25.074
28.358 " "	21.2453 "	25.082
28.287 " "	21.1833 "	25.113
57.170 " "	42.8366 "	25.072
		Mean, 25.088, ± .0044

The introduction of these figures into the subsequent calculations could not produce any appreciable result. They would practically vanish from the general mean. However, they serve here as confirmation of Stas' work.

† Aronstein's Translation, p. 214.

‡ Thomson's Annals of Philosophy, 1820, v. 15, p. 89.

132.700
132.780
132.790

Mean, 132.757, ± .019

Turner's work* closely resembles that of Berzelius. Silver was dissolved in nitric acid and precipitated as chloride. In experiments one, two, and three the mixture was evaporated and the residue fused. In experiment four the chloride was collected on a filter. A fifth experiment was made, but has been rejected as worthless.

The results were as follows: In a third column I put the quantity of AgCl proportional to 100 parts of Ag.

28.407	grains Ag gave		37.737	AgCl.	132.844
41.917	"	"	55.678	"	132.829
40.006	"	"	53.143	"	132.837
30.922	"	"	41.070	"	132.818

Mean, 132.832, ± .0038

The same general method of dissolving silver in nitric acid, precipitating, evaporating, and fusing without transfer of material was also adopted by Penny.† His results for 100 parts of silver are as follows, in parts of chloride:

132.836
132.840
132.830
132.840
132.840
132.830
132.838

Mean, 132.8363, ± .0012

In 1842 Marignac‡ found that 100 parts of silver formed 132.74 of chloride, but gave no available details. Later,||

* Phil. Transactions, 1829, 291.

† Phil. Transactions, 1839, 28.

‡ Ann. Chem. Pharm., 44, 21.

|| See Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.

in another series of determinations, he is more explicit, and gives the following data: The weighings were reduced to a vacuum standard.

79.853 grm. Ag gave	106.080 AgCl.	Ratio,	132.844
69.905 "	92.864 "		132.843
64.905 "	86.210 "		132.825
92.362 "	122.693 "		132.839
99.653 "	132.383 "		132.844
		Mean,	132.839, ± .0024

The above series all represent the synthesis of silver chloride. Maumené* made analyses of the compound, reducing it to metal in a current of hydrogen. His experiments make 100 parts of silver equivalent to chloride:

132.734
132.754
132.724
132.729
132.741

Mean, 132.7364, ± .0077

By Dumas† we have the following estimations:

9.954 Ag gave	13.227 AgCl.	Ratio,	132.882
19.976 "	26.542 "		132.869
		Mean,	132.8755, ± .0044

Finally, there are seven determinations by Stas,‡ made with his usual accuracy and with every precaution against error. In the first, second, and third, silver was heated in chlorine gas, and the synthesis of silver chloride thus effected directly. In the fourth and fifth silver was dissolved in nitric acid, and the chloride thrown down by passing hydrochloric acid gas over the surface of the solution. The whole was then evaporated in the same vessel, and the chloride fused, first in an atmosphere of hydrochloric acid,

* Ann. d. Chim. et d. Phys., (3,) 18, 49. 1846.
† Ann. Chem. Pharm., 113, 21. 1860.
‡ Aronstein's Translation, p. 171.

and then in a stream of air. The sixth synthesis was similar to these, only the nitric solution was precipitated by hydrochloric acid in slight excess, and the chloride thrown down was washed by repeated decantation. All the decanted liquids were afterwards evaporated to dryness, and the trace of chloride thus recovered was estimated in addition to the main mass. The latter was fused in an atmosphere of HCl. The seventh experiment was like the sixth, only ammonium chloride was used instead of hydrochloric acid. From 98.3 to 399.7 grammes of silver were used in each experiment, the operations were performed chiefly in the dark, and all weighings were reduced to vacuum. In every case the chloride obtained was beautifully white. The following are the results in chloride for 100 of silver:

	132.841
	132.843
	132.843
	132.849
	132.846
	132.848
	122.8417
Mean,	132.8445, ± .0008

We may now combine the means of these seven series, representing in all thirty-three experiments. One hundred parts of silver are equivalent to chlorine, as follows:

Berzelius	32.757, ± .0190
Turner	32.832, ± .0038
Penny	32.8363, ± .0012
Marignac	32.839, ± .0024
Maumené	32.7364, ± .0077
Dumas	32.8755, ± .0044
Stas	32.8445, ± .0008
General mean	32.8418, ± .0006

Here, again, we have a fine example of the evident compensation of errors among different series of experiments. We have also another tribute to the accuracy of Stas, since this general mean varies from the mean of his results only within the limits of his own variations.

The ratio between silver and potassium chloride, or, in other words, the weight of silver in nitric acid solution which can be precipitated by a known weight of KCl, has been fixed by Marignac and by Stas. Marignac,* reducing all weighings to vacuum, obtained these results. In the third column I give the weight of KCl proportional to 100 parts of Ag.

4.7238 grm. Ag =	3.2626 KCl.	69.067
21.725 "	15.001 "	69.050
21.759 "	15.028 "	69.066
21.909 "	15.131 "	69.063
22.032 "	15.216 "	69.063
25.122 "	17.350 "	69.063
		Mean, 69.062, ± .0017

Stas' experiments upon this ratio may be divided into two series.† In the first series the silver was slightly impure, but the impurity was of known quantity, and corrections could therefore be applied. In the second series pure silver was employed. The potassium chloride was from several different sources, and in every case was purified with the utmost care. From 10.8 to 32.4 grammes of silver were taken in each experiment, and the weighings were reduced to vacuum. The method of operation was, in brief, as follows: A definite weight of potassium chloride was taken, and the exact quantity of silver necessary, according to Prout's hypothesis, to balance it was also weighed out. The metal, with suitable precautions, was dissolved in nitric acid, and the solution mixed with that of the chloride. After double decomposition the trifling excess of silver remaining in the liquid was determined by titration with a normal solution of potassium chloride. One hundred parts of silver required the following of KCl:

* See Berzelius' Lehrbuch, 5th edition, Vol. 3, pp. 1192, 1193.

† Aronstein's Translation, pp. 250–257.

First Series.

69.105
69.104
69.103
69.104
69.102

Mean, 69.1036, $\pm$ .0003

Second Series.

69.105
69.099
69.107
69.103
69.103
69.105
69.104
69.099
69.1034
69.104
69.103
69.102
69.104
69.104
69.105
69.103
69,101
60.105
69.103

Mean, 69.1033, $\pm$ .0003

Now, combining the three series, with their thirty experiments, we get the following:

Marignac	69.062, $\pm$ .0017
Stas, 1st series	69.1036, $\pm$ .0003
Stas, 2d series	69.1033, $\pm$ .0003
General mean	69.1032, $\pm$ .0002

The quantity of silver chloride which can be formed from a known weight of potassium chloride has also been determined by Berzelius, Marignac, and Maumené. Berzelius* found that 100 parts of KCl were equivalent to 194.2 of

* Poggend. Annal., 8, 1. 1826.

AgCl; a value which, corrected for weighings in air, becomes 192.32. This experiment will not be included in our discussion.

In 1842 Marignac* published two determinations, with these results from 100 KCl:

192.33
192.34

Mean, corrected for weighing in air, 192.26, ± .003

In 1846 Marignac† published another set of results, as follows. The weighings were reduced to vacuum. The usual ratio is in the third column.

17.034 grm. KCl gave	32.761 AgCl.	192.327
14.427 "	27.749 "	192.341
15.028 "	28.910 "	192.374
15.131 "	29.102 "	192.334
15.216 "	29.271 "	192.370
	Mean,	192.349, ± .006

Three estimations of the same ratio were also made by Maumené,‡ as follows:

10.700 grm. KCl gave	20.627 AgCl.	192.776
10.5195 "	20.273 "	192.716
8.587 "	16.556 "	192.803
	Mean,	192.765, ± .017

The three series of ten experiments in all foot up thus:

Marignac, 1842	192.260, ± .003
" 1846	192.349, ± .006
Maumené	192.765, ± .017
General mean	192.294, ± .0029

These figures show clearly that the ratio which they represent is not of very high importance. It might be rejected altogether without impropriety, and is only retained for the

* Ann. Chem. Pharm., 44, 21. 1842.
† Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.
‡ Ann. d. Chim. et d. Phys., (3,) 18, 41. 1846.

sake of completeness. It will obviously receive but little weight in our final discussion.

In estimating the atomic weight of bromine the earlier experiments of Balard, Berzelius, Liebig, and Löwig may all be rejected. Their results were all far too low, probably because chlorine was present as an impurity in the materials employed. Wallace's determinations, based upon the analysis of arsenic tribromide, are tolerably good, but need not be considered here. In the present state of our knowledge, Wallace's analyses are better fitted for fixing the atomic weight of arsenic, and will, therefore, be discussed with reffference to that element.

The ratios with which we now have to deal are closely similar to those involving chlorine. In the first place there are the analyses of silver bromate by Stas.* In two careful experiments he found in this salt the following percentages of oxygen:

20.351
20.347

Mean, 20.349, ± .0014

There are also four analyses of potassium bromate by Marignac.† The salt was heated, and the percentage loss of oxygen determined. The residual bromide was feebly alkaline. We cannot place much reliance upon this series. The results are as follows:

28.7016
28.6496
28.6050
28.7460

Mean, 28.6755, ± .0207

When silver bromide is heated in chlorine gas, silver chloride is formed. In 1860 Dumas‡ employed this method

* Aronstein's Translation, pp. 200–206.

† See E. Mulder's Overzigt, p. 117; or Berzelius' Jahresbericht, 24, 72.

‡ Ann. Chem. Pharm., 113, 20.

for estimating the atomic weight of bromine. His results are as follows: In the third column I give the weight of AgBr equivalent to 100 parts of AgCl.

2.028 grm. AgBr gave	1.547 AgCl.		131.092
4.237 "	3.235 "		130.974
5.769 "	4.403 "		131.024
		Mean,	131.030, ± .023

This series is evidently of but little value.

But the two ratios upon which, in connection with Stas' analyses of silver bromate, the atomic weight of bromine chiefly depends are those which connect silver with the latter element directly and silver with potassium bromide.

Marignac,* to effect the synthesis of silver bromide, dissolved the metal in nitric acid, precipitated the solution with potassium bromide, washed, dried, fused, and weighed the product. The following quantities of bromine were found proportional to 100 parts of silver:

74.072
74.055
74.066

Mean, reduced to a vacuum standard, 74.077, ± .003

Much more elaborate determinations of this ratio are due to Stas.† In one experiment a known weight of silver was converted into nitrate, and precipitated in the same vessel by pure hydrobromic acid. The resulting bromide was washed thoroughly, dried, and weighed. In four other estimations the silver was converted into sulphate. Then a known quantity of pure bromine, as nearly as possible the exact amount necessary to precipitate the silver, was transformed into hydrobromic acid. This was added to the dilute solution of the sulphate, and, after precipitation was complete, the minute trace of an excess of silver in the clear supernatant fluid was determined. All weighings were re-

* E. Mulder's Overzigt, p. 116. Berzelius' Jahresbericht, 24, 72.

† Aronstein's Translation, pp. 154–170.

duced to a vacuum. From these experiments, taking both series as one, we get the following quantities of bromine corresponding to 100 parts of silver:

74.0830

74.0790
74.0795
74.0805
74.0830

Mean, 74.081, ± .0006

Combining this with Marignac's result, 74.077, ± .003, we get as a general mean the value 74.0809, ± .0006.*

The ratio between silver and potassium bromide was first accurately determined by Marignac.† I give, with his weighings, the quantity of KBr proportional to 100 parts of Ag:

2.131	grm. Ag =	2.351	KBr.	110.324
2.559	"	2.823	"	110.316
2.447	"	2.700	"	110.339
3.025	"	3.336	"	110.283
3.946	"	4.353	"	110.314
11.569	"	12.763	"	110.321
20.120	"	22.191	"	110.293

Mean, corrected for weighing in air, 110.343, ± .005

Stas,‡ working in essentially the same manner as when he fixed the ratio between potassium chloride and silver, obtained the following results:

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* O. W. Huntington, in his paper upon the atomic weight of cadmium, (Amer. Acad. Proc., 1881,) gives three analyses and three syntheses of silver bromide. These give a mean value of Ag : Br : : 100 : 74.064. This figure I record here in order that other chemists may not overlook the work of Mr. Huntington, although it came out too late for use in my own calculations.

† E. Mulder's Overzigt, p. 116. Berzelius' Jahresbericht, 24, 72.

‡ Aronstein's Translation, pp. 334–347.

110.361
110.360
110.360
110.342
110.346
110.338
110.360
110.336
110.344
110.332
110.343
110.357
110.334
110.335

Mean, 110.3463, ± .0020

Combining this with Marignac's mean result, 110.343, ± .005, we get a general mean of 110.3459, ± .0019.

The ratios upon which we must depend for the atomic weight of iodine are exactly parallel to those used for the determination of bromine.

To begin with, the percentage of oxygen in potassium iodate has been determined by Millon.* In three experiments he found:

22.46
22.49
22.47

Mean, 22.473, ± .005

Millon also estimated the oxygen in silver iodate, getting the following percentages:

17.05
17.03
17.06

Mean, 17.047, ± .005

The analysis of silver iodate has also been performed with extreme care by Stas.† From 76 to 157 grammes were used

* Ann. d. Chim. et d. Phys., (3,) 9, 400. 1843.
† Aronsteins' Translation, pp. 179–200.

in each experiment, the weights being reduced to a vacuum standard. As the salt could not be prepared in an absolutely anhydrous condition, the water expelled in each analysis was accurately estimated and the necessary corrections applied. In two of the experiments the iodate was decomposed by heat, and the oxygen given off was fixed upon a weighed quantity of copper heated to redness. Thus the actual weights, both of the oxygen and the residual iodide, were obtained. In a third experiment the iodate was reduced to iodide by a solution of sulphurous acid, and the oxygen was estimated only by difference. In the three percentages of oxygen given below the result of this analysis comes last. The figures for oxygen are as follows:

16.976
16.972
16.9761

Mean, 16.9747, $\pm$ .0009

This, combined with Millon's series above cited, gives us a general mean of 16.9771, $\pm$ .0009.

The ratio between silver and potassium iodide seems to have been determined only by Marignac,* and without remarkable accuracy. In five experiments 100 parts of silver were found equivalent to potassium iodide as follows:

1.616 grm. Ag =	2.483 KI.	Ratio,	153.651
2.503 "	3.846 "	"	153.665
3.427 "	5.268 "	"	152.720
2.141 "	3.290 "	"	153.667
10.821 "	16.642 "	"	153.794
		Mean,	153.6994, $\pm$ .0178

The synthesis of silver iodide has been effected by both Marignac and Stas. Marignac, in the paper above cited, gives these weighings. In the last column I add the ratio between iodine and 100 parts of silver:

15.000 grm. Ag gave	32.625 AgI.	117.500
14.790 "	32.170 "	117.512
18.545 "	40.339 "	117.519
	Mean, corrected for weighing in air,	117.5335, $\pm$ .0036

* Berzelius' Lehrbuch, 5th Ed., 3, 1196.

Stas* in his experiments worked after two methods, which gave, however, results concordant with each other and with those of Marignac.

In the first series of experiments Stas converted a known weight of silver into nitrate, and then precipitated with pure hydriodic acid. The iodide thus thrown down was washed, dried, and weighed without transfer. By this method 100 parts of silver were found to require of iodine:

117.529
117.536

Mean, 117.5325, ± .0024

In the second series a complete synthesis of silver iodide from known weights of iodine and metal was performed. The iodine was dissolved in a solution of ammonium sulphite, and thus converted into ammonium iodide. The silver was transformed into sulphate and the two solutions mixed. When the precipitate of silver iodide was completely deposited the supernatant liquid was titrated for the trifling excess of iodine which it always contained. As the two elements were weighed out in the ratio of 127 to 108, while the atomic weight of iodine is probably a little under 127, this excess is easily explained. From these experiments two sets of values were deduced; one from the weights of silver and iodine actually employed, the other from the quantity of iodide of silver collected. From the first set we have of iodine for 100 parts of silver:

117.5390
117.5380
117.5318
117.5430
117.5420
117.5300

Mean, 117.5373, ± .0015

From the weight of silver iodide actually collected we

* Aronstein's Translation, pp. 136, 152.

get as follows. For experiment number three in the above column there is no equivalent here:

117.529
117.531
117.539
117.538
117.530

Mean, 117.5334, ± .0014

Now, combining these several sets of results, we have the following general mean:

Marignac	117.5335, ± .0036
Stas, 1st series	117.5325, ± .0024
" 2d "	117.5373, ± .0015
" 3d "	117.5334, ± .0014
General mean	117.5345, ± .0009

One other comparatively unimportant iodine ratio remains for us to notice. Silver iodide, heated in a stream of chlorine, becomes converted into chloride; and the ratio between these two salts has been thus determined by Berzelius and by Dumas.

From Berzelius* we have the following data: In the third column I give the ratio between AgI and 100 parts of AgCl.

5.000 grm. AgI gave	3.062 AgCl.	163.292
12.212 "	7.4755 "	163.360
		Mean, 163.326, ± .023

Dumas'† results were as follows:

3.520 grm. AgI gave	2.149 AgCl.	163.793
7.011 "	4.281 "	163.770
		Mean, 163.782, ± .008

General mean from the combination of both series, 163.733, ± .0076.

We now come to the ratios connecting sulphur with silver

* Ann. d. Chim. et d. Phys., (2,) 40, 430. 1829.
† Ann. Chem. Pharm., 113, 28. 1860.

and chlorine. Other ratios have been applied to the determination of the atomic weight of sulphur, but they are hardly applicable here. The earlier results of Berzelius were wholly inaccurate, and his later experiments upon the synthesis of lead sulphate will be used in discussing the atomic weight of lead. Erdmann and Marchand determined the amount of calcium sulphate which could be formed from a known weight of pure Iceland spar; and later they made analyses of cinnabar, in order to fix the value of sulphur by reference to calcium and to mercury. Their results will be applied in this discussion towards ascertaining the atomic weights of the metals just named. For our present purposes only three ratios need be considered.

First in order let us take up the composition of silver sulphide, as directly determined by Dumas, Stas, and Cooke. Dumas'* experiments were made with sulphur which had been thrice distilled and twice crystallized from carbon disulphide. A known weight of silver was heated in a tube in the vapor of the sulphur, the excess of the latter was distilled away in a current of carbon dioxide, and the resulting silver sulphide was weighed.

I subjoin Dumas' weighings, and also the quantity of Ag_2S proportional to 100 parts of Ag, as deduced from them:

9.9393 grm. Ag	=	1.473	S.	Ratio,	114.820
9.962	"	1.4755	"	"	114.811
30.637	"	4.546	"	"	114.838
30.936	"	4.586	"	"	114.824
30.720	"	4.554	"	"	114.824
				Mean,	114.8234, ± .0029

Dumas used from ten to thirty grammes of silver in each experiment. Stas,† however, in his work, employed from sixty to two hundred and fifty grammes at a time. Three of Stas' determinations were made by Dumas' method, while in the other two the sulphur was replaced by pure sulphu-

* Ann. Chem. Pharm., 113, 24. 1860

† Aronstein's Translation, p. 179.

retted hydrogen. In all cases the excess of sulphur was expelled by carbon dioxide, purified with scrupulous care. Impurities in the dioxide may cause serious error. The five results come out as follows for 100 parts of silver:

114.854
114.853
114.854
114.851
114.849

Mean, 114.8522, ± .0007

The experiments made by Professor Cooke* with reference to this ratio were only incidental to his elaborate researches upon the atomic weight of antimony. They are interesting, however, for two reasons: they serve to illustrate the volatility of silver, and they represent, not syntheses, but reductions of the sulphide by hydrogen. Cooke gives three series of results. In the first the silver sulphide was long heated to full redness in a current of hydrogen. Highly concordant and at the same time plainly erroneous figures were obtained; the error being eventually traced to the fact that some of the reduced silver, although not heated to its melting point, was actually volatilized and lost. The second series, from reductions at low redness, are decidedly better. In the third series the sulphide was fully reduced below a visible red heat. Rejecting the first series we have from Cooke's figures in the other two the subjoined quantities of sulphide corresponding to 100 parts of silver:

7.5411 grm. Ag_2S lost	.9773 grm. S.	Ratio,	114.889
5.0364 "	.6524 "	"	114.882
2.5815 "	.3345 "	"	114.886
2.6130 "	.3387 "	"	114.892
2.5724 "	.3334 "	"	114.891
		Mean,	114.888, ± .0012

1.1357 grm. Ag_2S lost	.1465 S.	Ratio,	114.810
1.2936 "	.1670 "	"	114.823
		Mean,	114.8165, ± .0044

* Proc. American Acad. of Arts and Sciences, v. 12. 1877.

Now, combining all four series, we get the following results:

Dumas	114.8234, ± .0029
Stas	114.8522, ± .0007
Cooke's 2d	114.888, ± .0012
" 3d	114.8165, ± .0044
General mean	114.8581, ± .0006

Here again we encounter a curious and instructive compensation of errors, and another evidence of the accuracy of Stas.

The percentage of silver in silver sulphate has been determined by Struve and by Stas. Struve* reduced the sulphate by heating in a current of hydrogen, and obtained these results:

5.1860 grm. Ag_2SO_4	gave	3.5910 grm. Ag.		69.244 per cent.
6.0543	"	4.1922	"	69.243 "
8.6465	"	5.9858	"	69.228 "
11.6460	"	8.0608	"	69.215 "
9.1090	"	6.3045	"	69.212 "
9.0669	"	6.2778	"	69.239 "
			Mean,	69.230, ± .004

Stas,† working by essentially the same method, with from 56 to 83 grammes of sulphate at a time, found these percentages:

69.200
69.197
69.204
69.209
69.207
69.202

Mean, 69.203, ± .0012

Combining this mean with that from Struve's series we get a general mean of 69.205, ± .0011.

* Ann. Chem. Pharm., 80, 203. 1851.
† Aronstein's Translation, pp. 214-218.

The third and last sulphur ratio with which we have now to deal is one of minor importance. When silver chloride is heated in a current of sulphuretted hydrogen the sulphide is formed. This reaction was applied by Berzelius* to determining the atomic weight of sulphur. He gives the results of four experiments; but the fourth varies so widely from the others that I have rejected it. I have reason to believe that the variation is due, not to error in experiment, but to error in printing; nevertheless, as I am unable to track out the cause of the mistake, I must exclude the figures involving it entirely from our discussion.

The three available experiments, however, give the following results: The last column contains the ratio of silver sulphide to 100 parts of chloride.

6.6075	grm. AgCl gave	5.715	grm. Ag_2S.	86.478
9.2323	"	7.98325	"	86.471
10.1775	"	8.80075	"	86.472

Mean, 86.4737, ± .0015

We have also a single determination of this value by Svanberg and Struve.† After converting the chloride into sulphide they dissolved the latter in nitric acid. A trifling residue of chloride, which had been enclosed in sulphide, and so protected against change, was left undissolved. Hence a slight constant error probably affects this whole ratio. The experiment of Svanberg and Struve gave 86.472 per cent. of silver sulphide derived from 100 of chloride. If we assign this figure equal weight with the results of Berzelius, and combine, we get a general mean of 86.4733, ± .0011.

For sodium there are but two ratios of any definite value for present purposes. The early work of Berzelius we may disregard entirely, and confine ourselves to the consideration of the results obtained by Penny, Pelouze, Dumas, and Stas.

* Berzelius' Lehrbuch, 5th Ed., Vol. 3, p. 1187.

† Journ. für Prakt. Chem., 44, 320. 1848.

The percentage of oxygen in sodium chlorate has been determined only by Penny,* who used the same method which he applied to the potassium salt. Four experiments gave the following results:

45.060
45.075
45.080
45.067

Mean, 45.0705, ± .0029

The ratio between silver and sodium chloride has been fixed by Pelouze, Dumas, and Stas. Pelouze† dissolved a weighed quantity of silver in nitric acid, and then titrated with sodium chloride. Equivalent to 100 parts of silver he found of chloride:

54.158
54.125
54.139

Mean, 54.141, ± .0063

By Dumas‡ we have seven experiments, with results as follows: The third column gives the ratio between 100 of silver and NaCl.

2.0535 grm. NaCl	=	3.788 grm. Ag.		54.211
2.169	"	4.0095	"	54.097
4.3554	"	8.0425	"	54.155
6.509	"	12.0140	"	54.178
6.413	"	11.8375	"	54.175
2.1746	"	4.012	"	54.202
5.113	"	9.434	"	54.187
			Mean,	54.172, ± .0096

Stas,|| applying the method used in establishing the similar ratio for potassium chloride, and working with salt from

* Phil. Transactions, 1839, p. 25.
† Compt. Rend., 20, 1047. 1845.
‡ Ann. Chem. Pharm., 113, 31. 1860.
|| Aronstein's Translation, p. 274.

six different sources, found of sodium chloride equivalent to 100 parts of silver:

54.2093
54.2088
54.2070
54.2070
54.2070
54.2060
54.2076
54.2081
54.2083
54.2089
Mean, 54.2078, $\pm$ .0002

Now, combining these three series, we get the following result:

Pelouze	54.141,	$\pm$ .0063
Dumas	54.172,	$\pm$ .0096
Stas	54.2078,	$\pm$ .0002
General mean	54.2076,	$\pm$ .0002

Here the work of Stas is of such superior excellence that the other series might be completely rejected without appreciably affecting our calculations.

We have now before us the data establishing, with greater or less accuracy, twenty different ratios relating to the atomic weights of the seven elements under discussion. In these we are to discuss the results of about two hundred and fifty separate experiments. Before beginning upon our calculations we will tabulate our ratios, and number them for convenient future reference. Of course it will be understood that the probable errors given below relate to the last term of each proportion:

(1.)	Percentage of O in $KClO_3$	39.154,	$\pm$ .00038
(2.)	" " $KBrO_3$	28.6755,	$\pm$ .0207
(3.)	" " KIO_3	22.473,	$\pm$ .0050
(4.)	" " $NaClO_3$	45.0705,	$\pm$ .0029
(5.)	" " $AgClO_3$	25.0795,	$\pm$ .0010
(6.)	" " $AgBrO_3$	20.349,	$\pm$ .0014
(7.)	" " $AgIO_3$	16.9771,	$\pm$ .0009
(8.)	" Ag in Ag_2SO_4	69.205,	$\pm$ .0011

(9.) Ag : NaCl : : 100 : 54.2076, $\pm$ .0002
(10.) Ag : KCl : : 100 : 69.1032, $\pm$ .0002
(11.) Ag : KBr : : 100 : 110.3459, $\pm$ .0019
(12.) Ag : KI : : 100 : 153.6994, $\pm$ .0178
(13.) Ag : Cl : : 100 : 32.8418, $\pm$ .0006
(14.) Ag : Br : : 100 : 74.0809, $\pm$ .0006
(15.) Ag : I : : 100 : 117.5345, $\pm$ .0009
(16.) Ag : Ag_2S : : 100 : 114.8581, $\pm$ .0006
(17.) KCl : AgCl : : 100 : 192.294, $\pm$ .0029
(18.) AgCl : AgBr : : 100 : 131.030, $\pm$ .023
(19.) AgCl : AgI : : 100 : 163.733, $\pm$ .0076
(20.) AgCl : Ag_2S : : 100 : 86.4733, $\pm$ .0011

Now, from ratios 1 to 7 inclusive, we can at once, by applying the known atomic weight of oxygen, deduce the molecular weights of seven haloid salts. Let us consider the first calculation somewhat in detail.

Potassium chlorate yields 39.154 per cent. of oxygen and 60.846 per cent. of residual chloride. For each of these quantities the probable error is $\pm$ .00038. The atomic weight of oxygen is 15.9633, $\pm$ .0035, so that the value for three atoms becomes 47.8899, $\pm$ .0105. We have now the following simple proportion: 39.154 : 60.846 : : 47.8899 : x, = the molecular weight of potassium chloride, = 74.4217. The probable error being known for the first, second, and third term of this proportion, we can easily find that of the fourth term by the formula given in our introduction. It comes out $\pm$ .0164. By this method we obtain the following series of values, which may conveniently be numbered consecutively with the foregoing ratios:

(21.)	KCl,	from (1.) =	74.4217,	$\pm$ .0164
(22.)	KBr,	" (2.) =	119.117,	$\pm$ .0962
(23.)	KI,	" (3.) =	165.210,	$\pm$ .0529
(24.)	NaCl,	" (4.) =	58.366,	$\pm$ .0137
(25.)	AgCl,	" (5.) =	143.062,	$\pm$ .0320
(26.)	AgBr,	" (6.) =	187.453,	$\pm$ .0432
(27.)	AgI,	" (7.) =	234.195,	$\pm$ .0530

With the help of these molecular weights we are now able to calculate eight independent values for the atomic weight of silver:

First,	from	(10)	and	(21,)	Ag	= 107.696, ± .024
Second,	"	(11)	"	(22,)	"	= 107.948, ± .087
Third,	"	(12)	"	(23,)	"	= 107.488, ± .037
Fourth,	"	(9)	"	(24,)	"	= 107.671, ± .025
Fifth,	"	(13)	"	(25,)	"	= 107.694, ± .024
Sixth,	"	(14)	"	(26,)	"	= 107.681, ± .025
Seventh,	"	(15)	"	(27,)	"	= 107.659, ± .024
Eighth,	"	(8)	"	(16,)	"	= 107.712, ± .025
		General mean,			"	= 107.675, ± .0096

It is noticeable that six of these values agree very well. The second and third, however, diverge widely from the average, but in opposite directions; they have, moreover, high probable errors, and consequently little weight. Of these two, one represents little and the other none of Stas' work. Their trifling influence upon our final results becomes curiously apparent in the series of silver values given a little further along.

When we consider closely, in all of its bearings, any one of the values just given, we shall see that for certain purposes it must be excluded from our general mean. For example, the first is derived partly from the ratio between silver and potassium chloride. From this ratio, the atomic weight of one substance being known, we can deduce that of the other. We have already used it in ascertaining the atomic weight of silver, and the value thus obtained is included in our general mean. But if from it we are to determine the molecular weight of potassium chloride, we must use a silver value derived from other sources only, or we should be assuming a part of our result in advance. In other words, we must now use a general mean for silver from which this ratio with reference to silver has been rejected. Hence the following series of silver values, which are lettered for reference:

A.	General mean from all eight	107.675, ± .0096
B.	" rejecting the first	107.671, ± .0105
C.	" " second	107.671, ± .0097
D.	" " third	107.679, ± .0100
E.	" " fourth	107.675, ± .0104
F.	" " fifth	107.671, ± .0105
G.	" " sixth	107.674, ± .0104
H.	" " seventh	107.678, ± .0105
I.	" " eighth	107.679, ± .0104

These values are essentially the same, both in magnitude and in weight. For all practical purposes any one of them is as good as any other. Still, on theoretical grounds, it may be well to keep them distinct and separate in the remainder of this discussion.

We are now in a position to determine more closely the molecular weights of the haloid salts which we have already been considering.

For silver chloride, still employing the formula for the probable error of the last term of a proportion, we get the following values:

From (5)	AgCl	= 143.062, ± .032
From (13) and (F)	"	= 143.032, ± .014
From (17) and (21)	"	= 143.108, ± .034
From (18) and (26)	"	= 143.061, ± .041
From (19) and (27)	"	= 143.035, ± .033
General mean	"	= 143.045, ± .0108

Subtracting from this the atomic weight of silver, 107.675, ± .0096, we get for the atomic weight of chlorine, Cl = 35.370, ± .014.

For silver bromide we have these results:

From (6)	AgBr	= 187.453, ± .043
From (14) and (G)	"	= 187.440, ± .018
From (18) and (25)	"	= 187.454, ± .053
General mean	"	= 187.443, ± .016

Hence, using the general mean for silver as above, Br = 79.768, ± .019.

Silver iodide comes out as follows:

From (7)	AgI	= 234.195, ± .053
From (15) and (H)	"	= 234.237, ± .023
From (19) and (25)	"	= 234.240, ± .054
General mean	"	= 234.232, ± .019

Hence I = 126.557, ± .022.

For the molecular weight of sodium chloride we have:

From (4)	NaCl	= 58.366, ± .0137
From (9) and (E)	"	= 58.368, ± .0056
General mean	"	= 58.3676, ± .0052

Hence, if chlorine = 35.370, ± .014, then Na = 22.998, ± .011.

For potassium chloride:

From (1)	KCl	= 74.4217, ± .016
From (10) and (B)	"	= 74.4041, ± .007
From (17) and (25)	"	= 74.3975, ± .017
General mean	"	= 74.4057, ± .0062

For potassium bromide we get:

From (2)	KBr	= 119.117, ± .096
From (11) and (C)	"	= 118.810, ± .0118
General mean	"	= 118.815, ± .0117

And for potassium iodide:

From (3)	KI	= 165.210, ± .053
From (12) and (D)	"	= 165.502, ± .029
General mean	"	= 165.432, ± .026

Now, taking the molecular weights of these three potassium salts in connection with the atomic weights just found for chlorine, bromine, and iodine, we get these values for potassium:

From the chloride	K	= 39.036, ± .016
From the bromide	"	= 39.047, ± .022
From the iodide	"	= 38.875, ± .034
General mean	"	= 39.019, ± .012

Finally, the three sulphur ratios give us three estimates for the atomic weight of sulphur. In the third of these I have applied the "A" value for silver and the general mean for silver chloride:

From (8) and (1)	S	= 31.968, ± .014
From (16) and (1)	"	= 31.995, ± .032
From (20)	"	= 32.041, ± .028
General mean	"	= 31.984, ± .012

We may now appropriately compare the results of this

discussion with the atomic weights deduced by Stas from his own experiments only. His values are given under two headings: one for oxygen = 16, the other for O = 15.96. As we have been using the figure 15.9633 for oxygen, here is at the outset a discrepancy. Starting from this value we found:

Ag	=	107.675, ± .0096
Cl	=	35.370, ± .014
Br	=	79.768, ± .019
I	=	126.557, ± .022
Na	=	22.998, ± .011
K	=	39.019, ± .012
S	=	31.984, ± .012

If we assume 16 to be the true figure for oxygen, we get the following results, which I have placed in a column parallel with the values found by Stas:

	The New Values.	*Stas.*	*Differences.*
Silver	107.923	107.930	.007
Chlorine	35.451	35.457	.006
Bromine	79.951	79.952	.001
Iodine	126.848	126.850	.002
Sodium	23.051	23.043	.009
Potassium	39.109	39.137	.028
Sulphur	32.058	32.074	.016

These differences are insignificant. No other criticism could more severely test the character of Stas' work, or more definitely illustrate his magnificent accuracy of manipulation.

NITROGEN.

The atomic weight of nitrogen has been determined from the density of the gas, from the ratio between ammonium chloride and silver, and from the composition of certain nitrates.

Upon the density of nitrogen a great many experiments have been made. In early times this constant was determined by Biot and Arago, Thomson, Dulong and Berzelius, Lavoisier, and others. But all of these investigations may be disregarded as of insufficient accuracy; and, as in the case of oxygen, we need consider only the results obtained by Dumas and Boussingault, and by Regnault.

Taking air as unity, Dumas and Boussingault* found the density of nitrogen to be—

.970
.972
.974

Mean, .972, ± .00078

For hydrogen, as was seen in our discussion of the atomic weight of oxygen, the same investigators found a mean of .0693, ± .00013. Upon combining this with the above nitrogen mean, we find for the atomic weight of the latter element, N = 14.026, ± .0295.

By Regnault† much closer work was done. He found the density of nitrogen to be as follows:

.97148
.97148
.97154
.97155
.97108
.97108

Mean, .97137, ± .000062

* Compt. Rend., 12, 1005. 1841.
† Compt. Rend., 20, 975. 1845.

For hydrogen, Regnault's mean value is .069263, ± .000019. Hence, combining as before, N = 14.0244, ± .0039.*

The value found by combining both series of experiments is N = 14.0244, ± .0039.

In discussing the more purely chemical ratios for establishing the atomic weight of nitrogen, we may ignore, for the present, the researches of Berzelius, of Anderson, and of Svanberg. These chemists experimented chiefly upon lead nitrate, and their work is consequently now of greater value for fixing the atomic weight of lead. Their results will be duly considered in the proper connection further on.

The ratio between ammonium chloride and silver has been determined by Pelouze, by Marignac, and by Stas. The method of working is essentially that adopted in the similar experiments with the chlorides of sodium and potassium.

For the ammonium chloride equivalent to 100 parts of silver, Pelouze† found:

49.556
49.517

Mean, 49.5365, ± .013

Marignac‡ obtained the following results. The usual ratio for 100 parts of silver is given also:

8.063 grm. Ag	=	3.992 grm. NH_4Cl.		49.510
9.402	"	4.656	"	49.521
10.339	"	5.120	"	49.521
12.497	"	6.191	"	49.540
11.337	"	5.617	"	49.546
11.307	"	5.595	"	49.483
4.326	"	2.143	"	49.538

Mean, 49.523, ± .0055

* Professor Le Conte, in his corrections of Regnault's calculations, already cited in a foot note to the chapter on oxygen, finds for the density of nitrogen the value 0.971346. Hence N = 14.0225. This correction is very slight, but it should be considered in any future revision of the atomic weights.

† Compt. Rend., 20, 1047. 1845.

‡ Berzelius' Lehrbuch, 5th Ed., 3d v., 1184, 1185.

But neither of these series can for a moment compare with that of Stas.* He used from 12.5 to 80 grammes of silver in each experiment, reduced his weighings to a vacuum standard, and adopted a great variety of precautions to ensure accuracy. He found for every 100 parts of silver the following quantities of NH_4Cl:

49.600
49.599
49.597
49.598
49.597
49.593
49.597
49.5974
49.602
49.597
49.598
49.592

Mean, 49.5973, ± .0005

Now, combining these three series, we get:

Pelouze	49.5365, ± .013
Marignac	49.523, ± .0055
Stas	49.5973, ± .0005
General mean	49.597, ± .0005

The quantity of silver nitrate which can be formed from a known weight of metallic silver has been determined by Penny, by Marignac, and by Stas. Penny† dissolved silver in nitric acid in a flask, evaporated to dryness without transfer, and weighed. One hundred parts of silver thus gave of nitrate:

157.430
157.437
157.458
157.440
157.430
157.455

Mean, 157.4417, ± .0033

* Aronstein's Translation, pp. 56–58.
† Phil. Trans., 1839.

Marignac's* results were as follows. In the third column they are reduced to the common standard of 100 parts of silver:

68.987	grm. Ag gave	108.608	grm. $AgNO_3$.		157.433
57.844	"	91.047	"		157.401
66.436	"	104.592	"		157.433
70.340	"	110.718	"		157.404
200.000	"	314.894	"		157.447
				Mean,	157.4236, ± .0061

Stas,† employing from 77 to 405 grammes of silver in each experiment, made two different series of determinations at two different times. The silver was dissolved with all the usual precautions against loss and against impurity, and the resulting nitrate was weighed, first after long drying without fusion just below its melting point; and again, fused. Between the fused and the unfused salt there was in every case a slight difference in weight, the latter giving a maximum and the former a minimum value.

In Stas' first series there are eight experiments; but the seventh he himself rejects as inexact. The values obtained for the nitrate from 100 parts of silver are given below in two columns, representing the two conditions in which the salt was weighed. The general mean given at the end I have deduced from the means of the two columns considered separately:

Unfused.	*Fused.*
157.492	157.474
157.510	157.481
157.485	157.477
157.476	157.471
157.478	157.470
157.471	157.463
157.488	157.469
Mean, 157.4857	Mean, 157.472

General mean, 157.474, ± .0014

* Berzelius' Lehrbuch, 5th Ed., 3, pp. 1184, 1185.

† Aronstein's Translation, pp. 305 and 315.

In the later series there are but two experiments, as follows:

Unfused.	*Fused.*
157.4964	157.488
157.4940	157.480
Mean, 157.4952	Mean, 157.484

General mean, 157.486, ± .0003

Now, to combine all four sets of results:

Penny	157.4417, ± .0033
Marignac	157.4236, ± .0061
Stas, 1st series	157.4740, ± .0014
Stas, 2d series	157.4860, ± .0003
General mean	157.479, ± .0003

For the direct ratio between silver nitrate and silver chloride there are two series of estimations. A weighed quantity of nitrate is easily converted into chloride, and the weight of the latter ascertained. In two experiments Turner* found of chloride from 100 parts of nitrate:

84.357
84.389

Mean, 84.373, ± .011

Penny,† in five determinations, found the following percentages:

84.370
84.388
84.377
84.367
84.370

Mean, 84.3744, ± .0025

The general mean from both series is 84.3743, ± .0025.

The ratio directly connecting silver nitrate with ammonium chloride has been determined only by Stas.‡ The

* Phil. Trans., 1833, 537.
† Phil. Trans., 1839.
‡ Aronstein's Translation, p. 309.

usual method of working was followed; namely, nearly equivalent quantities of the two salts were weighed out, the solutions mixed, and the slight excess of one estimated by titration. In four experiments 100 parts of silver nitrate were found equivalent to chloride of ammonium as follows:

31.489
31.490
31.487
31.486

Mean, 31.488, ± .0006

The similar ratio between potassium chloride and silver nitrate has been determined by both Marignac and Stas.

Marignac* gives the following weights. I add the quantity of KCl proportional to 100 parts of $AgNO_3$:

1.849 grm. KCl		4.218 grm. $AgNO_3$.		43.836
2.473	"	5.640	"	43.848
3.317	"	7.565	"	43.847
2.926	"	6.670	"	43.868
6.191	"	14.110	"	43.877
4.351	"	9.918	"	43.870
			Mean,	43.858, ± .0044

Stas'† results are given in three series, representing silver nitrate from three different sources. In the third series the nitrate was weighed in vacuo, while for the other series this correction was applied in the usual way. For the KCl equivalent to 100 parts of $AgNO_3$ Stas found:

First Series.

43.878
43.875
43.875
43.874

Mean, 43.8755, ± .0005

* Berzelius' Lehrbuch, 5th Ed., 3d vol., 1184, 1185.
† Aronstein's Translation, p. 308.

Second Series.

43.864
43.869
43.876

Mean, 43.8697, ± .0023

Third Series.

43.894
43.878
43.885

Mean, 43.8857, ± .0031

Combining all four series we have:

Marignac	43.858, ± .0044
Stas, 1st series	43.8755, ± .0005
" 2d "	43.8697, ± .0023
" 3d "	43.8857, ± .0031
General mean	43.8715, ± .0004

There have also been determined by Penny and by Stas a series of ratios connecting the alkaline chlorides and chlorates with the corresponding nitrates. One of these, relating to the lithium salts, will be studied further on with reference to that metal.

The general method of working upon these ratios is due to Penny.* Applied to the ratio between the chloride and nitrate of potassium it is as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat. Then, upon evaporating to dryness over a sand bath, the nitrate is brought into weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which had been mechanically carried over is recovered and also taken into account. In another series of experiments the nitrate was taken, and by pure hydrochloric acid converted into chloride; the process being the same. In the following columns of figures I

* Phil. Trans., 1839.

have reduced both series to one standard; namely, so as to express the number of parts of nitrate corresponding to 100 of chloride:

First Series.—KCl treated with HNO_3.

135.639
135.637
135.640
135.635
135.630
135.640
135.630

Mean, 135.636, ± .0011

Second Series.—KNO_3 treated with HCl.

135.628
135.635
135.630
135.641
135.630
135.635
135.630

Mean, 153.633, ± .0011

Stas* results are as follows:

135.643
135.638
135.647
135.649
135.640
135.645
135.655

Mean, 135.6453, ± .0014

These figures by Stas represent weighings in the air. Reduced to a vacuum standard this mean really becomes 135.6423.

Now, combining, we have:

Penny, 1st series	135.636,	± .0011
" 2d "	135.633,	± .0011
Stas	135.6423,	± .0014
General mean	135.6363,	± .0007

* Aronstein's Translation, p. 270.

By the same general process Penny* determined how much potassium nitrate could be formed from 100 parts of chlorate. He found as follows:

82.505
82.497
82.498
82.500

Mean, 82.500, ± .0012

For 100 parts of sodium chlorate he found of nitrate:

79.875
79.882
79.890

Mean, 79.8823, ± .0029

For the ratio between the chloride and nitrate of sodium Penny made two sets of estimations as in the case of potassium salts. The subjoined figures give the amount of nitrate equivalent to 100 parts of chloride:

First Series.—$NaCl$ treated with HNO_3.

145.415
145.408
145.420
145.424
145.410
145.418
145.420

Mean, 145.4164, ± .0015

Second Series.—$NaNO_3$ treated with HCl.

145.419
145.391
145.412
145.415
145.412
145.412

Mean, 145.410, ± .0026

* Phil. Trans., 1839.

Stas* gives the following series:

145.453
145.468
145.465
145.469
145.443

Mean, after reducing to vacuum standard, 145.4526, ± .0030

Combining, we have as follows:

Penny, 1st series	145.4164, ± .0015
" 2d "	145.410, ± .0026
Stas	145.4526, ± .0030
General mean	145.4185, ± .0012

We have now, apart from the determinations of gaseous density, nine ratios, representing one hundred and fourteen experiments from which to calculate the atomic weight of nitrogen. Let us first collect and number these ratios:

(1.) $Ag : AgNO_3 :: 100 : 157.479$, ± .0003
(2.) $AgNO_3 : AgCl :: 100 : 84.3743$, ± .0025
(3.) $AgNO_3 : KCl :: 100 : 43.8715$, ± .0004
(4.) $AgNO_3 : NH_4Cl :: 100 : 31.488$, ± .0006
(5.) $Ag : NH_4Cl :: 100 : 49.597$, ± .0005
(6.) $KCl : KNO_3 :: 100 : 135.6363$, ± .0007
(7.) $KClO_3 : KNO_3 :: 100 : 82.500$, ± .0012
(8.) $NaCl : NaNO_3 :: 100 : 145.4185$, ± .0012
(9.) $NaClO_3 : NaNO_3 :: 100 : 79.8823$, ± .0029

From these ratios we are now able to deduce the molecular weight of ammonium chloride and of the three nitrates named in them. For these calculations we may use the already determined atomic weights of silver, oxygen, potassium, sodium, and chlorine, and the molecular weights of silver chloride and sodium chloride. These two molecular weights involve, respectively, the most probable values for silver, sodium, and chlorine. We cannot, however, appropriately use the directly determined molecular weight of potassium chloride, since the most probable value for the

* Aronstein's Translation, p. 278.

atomic weight of potassium is only in part derived from that salt. The following are the values which we shall employ:

Ag	= 107.675,	± .0096
K	= 39.019,	± .012
Na	= 22.998,	± .011
Cl	= 35.370,	± .014
O_3	= 47.8899,	± .0105
AgCl	= 143.045,	± .0108
NaCl	= 58.3676,	± .0052

Now, from ratio number five we can get the molecular weight of ammonium chloride, NH_4Cl = 53.4048, ± .0048, and N = 14.0336, ± .0153.

From ratio number four an independent value for nitrogen can be calculated, namely, N = 14.0330, ± .015.

For the molecular weight of silver nitrate three values are deducible, namely:

From (1)............	$AgNO_3$	= 169.5655, ± .0151
From (2)............	"	= 169.5362, ± .0138
From (3)............	"	= 169.5612, ± .0429
General mean .	"	= 169.5489, ± .0099

Hence N = 13.9840, ± .0174.

The molecular weight of potassium nitrate is twice calculable, as follows:

From (6)............	KNO_3	= 100.8985, ± .0255
From (7)............	"	= 100.8801, ± .0178
General mean..	"	= 100.8863, ± .0146

And N = 13.9774, ± .0216.

So also for sodium nitrate we have:

From (8)............	$NaNO_3$	= 84.8773, ± .0076
From (9)............	"	= 84.8809, ± .0099
General mean..	"	= 84.8785, ± .0060

And N = 13.9906, ± .0163.

We have now before us six estimates of the atomic weight of nitrogen. It only remains for us to combine these after

the usual method, as follows, in order to obtain the most probable value:

1.	From specific gravity of N	N =	14.0244,	± .0039
2.	" ammonium chloride	" =	14.0336,	± .0153
3.	" ratio number four	" =	14.0330,	± .0150
4.	" silver nitrate	" =	13.9840,	± .0174
5.	" potassium nitrate	" =	13.9774,	± .0216
6.	" sodium nitrate	" =	13.9906,	± .0163
	General mean	" =	14.0210,	± .0035

If oxygen is 16, this becomes 14.0291. Stas found N = 14.044. The difference is .015, showing a remarkably close agreement.

CARBON.

Although there is a large mass of material relating to the atomic weight of carbon, much of it may be summarily set aside as having no value for present purposes. The density of carbon dioxide, which has been scrupulously determined by many investigators,* leads to no safe estimate of the constant under consideration. The numerous analyses of hydrocarbons, like the analyses of naphthalene by Mitscherlich, Woskresensky, Fownes, and Dumas, give results scarcely more satisfactory. In short, all the work done upon the atomic weight of carbon before the year 1840 may be safely rejected as unsuited to the present requirements of exact science. As for methods of estimation we need consider but three, as follows:

First.—The analysis of organic salts of silver.

Second.—The determination of the weight of carbon dioxide formed by the combustion of a known weight of carbon.

* Notably by Lavoisier, Biot and Arago, De Saussure, Dulong and Berzelius, Buff, Von Wrede, Regnault, and Marchand. For details, Van Geuns' monograph may be consulted.

Third.—The method of Stas, by the combustion of carbon monoxide.

The first of these methods, which is also the least accurate, was employed by Liebig and Redtenbacher* in 1840. They worked with the acetate, tartrate, racemate, and malate of silver, making five ignitions of each salt, and determining the percentage of metal. From one to nine grammes of material were used in each experiment.

In the acetate the following percentages of silver were found:

64.615
64.624
64.623
64.614
64.610

Mean, 64.6172, ± .0018

After applying corrections for weighing in air this mean becomes 64.6065.

In the tartrate the silver came out as follows:

59.297
59.299
59.287
59.293
59.293

Mean, 59.2938, ± .0014
Or, reduced to a vacuum, 59.2806

In the racemate we have:

59.290
59.292
59.287
59.283
59.284

Mean, 59.2872, ± .0012
Or, corrected, 59.2769

* Ann. Chem. Pharm., 38, 137. Mem. Chem. Soc., 1, 9. Phil. Mag., (3,) 19, 210.

And from the malate:

61.996
61.972
62.015
62.059
62.011
Mean, 62.0106, $\pm$ .0096
Or, corrected, 62.0016

Now, applying to these mean results the atomic weights already found for oxygen and silver, we get the following values for carbon:

From the acetate	C =	12.0306, $\pm$ .0047
" tartrate	" =	12.0356, $\pm$ .0064
" racemate	" =	12.0413, $\pm$ .0063
" malate	" =	12.0408, $\pm$ .0054
General mean	" =	12.0363, $\pm$ .0028

Now these results, although remarkably concordant, are by no means unimpeachable. They involve two possible sources of constant error, namely, impurity of material and the volatility of the silver. These objections have both been raised by Stas, who found that the silver tartrate, prepared as Liebig and Redtenbacher prepared it, always carried traces of the nitrate, and that he, by the ignition of that salt, could not get results at all agreeing with theirs. In the case of the acetate a similar impurity would lower the percentage of silver, and thus both sources of error would reinforce each other and make the atomic weight of carbon come out too high. With the three other salts the two sources of error act in opposite directions, although the volatility of the silver is probably far greater in its influence than the impurity. Even if we had no other data relating to the atomic weight of carbon, it would be clear from these facts that the results obtained by Liebig and Redtenbacher must be decidedly in excess of the true figure.

A different method of dealing with organic silver salts was adopted by Maumené,* in 1846, for the purpose of estab-

* Ann. d. Chim. et d. Phys., (3.) 18, 41.

lishing, by reference to carbon, the atomic weight of silver. We will simply reverse his results and apply them to the atomic weight of carbon. He effected the combustion of the acetate and the oxalate of silver, and, by weighing both the residual metal and the carbon dioxide formed, he fixed the ratio between these two substances. In the case of the acetate his weighings show that for every gramme of metallic silver the weights of CO_2 were produced, which are shown in the third column:

8.083 grm. Ag =	6.585 grm. CO_2.	.8147
11.215 "	9.135 "	.8136
14.351 "	11.6935 "	.8148
9.030 "	7.358 "	.8148
20.227 "	16.475 "	.8145
	Mean,	.81448

The oxalate of silver, ignited by itself, decomposes too violently to give good results; and for this reason it was not used by Liebig and Redtenbacher. Maumené, however, found that when the salt was mixed with sand the combustion could be tranquilly effected. The oxalate employed, however, with the exception of the sample represented in the last experiment of the series, contained traces of nitrate, so that these results involve slight errors. For each gramme of silver the appended weights of CO_2 were obtained:

14.299 grm. Ag =	5.835 grm. CO_2.	.4081
17.754 "	7.217 "	.4059
11.550 "	4.703 "	.4072
10.771 "	4.387 "	.4073
8.674 "	3.533 "	.4073
11.4355 "	4.658 "	.4073
	Mean,	.40718

Now, one of these salts being formed by a bivalent and the other by a univalent acid, we have to reduce both to a common standard. Doing this, we have the following results for the ratio between the atomic weight of silver and the molecular weight of CO_2; if Ag = 1.00,

From the acetate, CO_2	$= .40724$,	$\pm .000076$
" oxalate, "	$= .40718$,	$\pm .000185$
General mean, "	$= .40723$,	$\pm .000071$

Here the slight error due to the impurity of the oxalate becomes of such trifling weight that it practically vanishes.

From these data, if Ag $= 107.675$, $\pm .0096$, $CO_2 = 43.8485$, $\pm .0086$.

Hence C $= 11.9219$, $\pm .0111$.

As has already been said, the volatility of silver renders all the foregoing results more or less uncertain. Far better figures are furnished by the combustion of carbon directly, as carried out by Dumas and Stas* in 1840 and by Erdmann and Marchand† in 1841. In both investigations weighed quantities of diamond, of natural graphite, and of artificial graphite were burned in oxygen, and the amount of dioxide produced was estimated by the usual methods. The graphite employed was purified with extreme care by treatment with strong nitric acid and by fusion with caustic alkali. I have reduced all the published weighings to a common standard, so as to show in the third column the amount of oxygen which combines with a unit weight (say one gramme) of carbon. Taking Dumas and Stas' results first in order we have from natural graphite:

1.000 grm. C gave	3.671 grm. CO_2.	2.6710
.998 "	3.660 "	2.6673
.994 "	3.645 "	2.6670
1.216 "	4.461 "	2.6686
1.471 "	5.395 "	2.6676
	Mean,	2.6683, $\pm .0005$

With artificial graphite:

.992 grm. C gave	3.642 grm. CO_2.	2.6714
.998 "	3.662 "	2.6682
1.660 "	6.085 "	2.6654
1.465 "	5.365 "	2.6744
	Mean,	2.66985, $\pm .0013$

* Compt. Rend., 11, 991–1008. Ann. Chim. Phys., (3,) 1, 1.

† Journ. f. Prakt. Chem., 23, 159.

And with diamond:

.708 grm. C gave	2.598 grm. CO_2.		2.6695
.864 "	3.1675 "		2.6661
1.219 "	4.465 "		2.6628
1.232 "	4.519 "		2.6680
1.375 "	5.041 "		2.6662
		Mean,	2.6665, ± .0007

Erdmann and Marchand's figures for natural graphite give the following results:

1.5376 grm. gave	5.6367 grm. CO_2.	2.6659
1.6494 "	6.0384 "	2.6609
1.4505 "	5.31575 "	2.6647

In one experiment 1.8935 grm. of artificial graphite gave 6.9355 grm. CO_2. Ratio for O, 2.6628. This, combined with the foregoing series, gives a mean of 2.6636, ± .0007.

With diamond they found:

.8052 grm. gave	2.9467 grm. CO_2.		2.6596
1.0858 "	3.9875 "		2.6632
1.3557 "	4.9659 "		2.6629
1.6305 "	5.97945 "		2.6673
.7500 "	2.7490 "		2.6653
		Mean,	2.6637, ± .0009

Now, combining all these series, we get the following result:

Dumas and Stas, 1st set	2.6683,	± .0005
" 2d "	2.66985,	± .0013
" 3d "	2.6665,	± .0007
Erdmann and Marchand, 1st	2.6636,	± .0007
" 2d	2.6637,	± .0009
General mean	2.66655,	± .0003

Hence, if O = 15.9633, ± .0035, C = 11.973, ± .0030.

Another very exact method for determining the atomic weight of carbon was employed by Stas* in 1849. Carefully purified carbon monoxide was passed over a known weight

* Bull. Acad. Bruxelles, 1849, (1,) 31.

of copper oxide at a red heat, and both the residual metal and the carbon dioxide formed were weighed. The weighings were reduced to a vacuum standard, and in each experiment a quantity of copper oxide was taken representing from eight to twenty-four grammes of oxygen. The method, as will at once be seen, is in all essential features similar to that usually employed for determining the composition of water. The figures in the third column, deduced from the weights given by Stas, represent the quantity of carbon monoxide corresponding to one gramme of oxygen:

9.265 grm. O =	25.483 CO_2.	1.75046
8.327 "	22.900 "	1.75010
13.9438 "	38.351 "	1.75040
11.6124 "	31.935 "	1.75008
18.763 "	51.6055 "	1.75039
19.581 "	53.8465 "	1.74994
22.515 "	61.926 "	1.75043
24.360 "	67.003 "	1.75053
	Mean,	1.75029, ± .00005

Hence the molecular weight of carbon monoxide is 27.9404, ± .0062. And C = 11.9771, ± .0071.

Now, in order to complete our discussion, we must combine the four values we have found for carbon:

1. By Liebig and Redtenbacher	C =	12.0363, ± .0028
2. By Maumené's figures	" =	11.9219, ± .0111
3. By combustion of carbon	" =	11.9730, ± .0030
4. By Stas' method	" =	11.9771, ± .0071
General mean	" =	12.0021, ± .0019

But values one and two are hardly reliable enough to be included in our final estimate. They involve dangerous constant errors, and ought, therefore, to be disregarded. Rejecting them altogether, and taking a general mean from values three and four, we get for the most probable figure for the atomic weight of carbon, C = 11.9736, ± .0028. If oxygen is 16, then carbon becomes 12.0011. In other words, the ratio between oxygen and carbon is almost exactly 16 to 12.

BARIUM.

For determining the atomic weight of barium we have a series of six ratios, established by the labors of Berzelius, Turner, Struve, Pelouze, Marignac, and Dumas. Andrews* and Salvetat,† in their papers upon this subject, gave no details nor weighings; and, therefore, their work may be properly disregarded. First in order in point of importance, if not first chronologically, is the ratio between silver and anhydrous barium chloride, as determined by Pelouze, Marignac, and Dumas.

Pelouze,‡ in 1845, made the three subjoined estimations of this ratio, using his well known volumetric method. A quantity of pure silver was dissolved in nitric acid, and the amount of barium chloride needed to precipitate it was accurately ascertained. In the last column I give the quantity of barium chloride proportional to 100 parts of silver:

3.860 grm. $BaCl_2$ ppt.	4.002 grm. Ag.			96.452
5.790 "	6.003 "			96.452
2.895 "	3.001 "			96.468
			Mean,	96.4573, ± .0036

Essentially the same method was adopted by Marignac|| in 1848. His experiments were made upon four samples of barium chloride, as follows. A, commercial barium chloride, purified by recrystallization from water. B, the same salt, calcined, redissolved in water, the solution saturated with carbonic acid, filtered, and allowed to crystallize. C, the preceding salt, washed with alcohol, and again recrystallized. D, the same, again washed with alcohol. For 100 parts of silver the following quantities of chloride were required:

* Chemical Gazette, October, 1852.

† Compt. Rend., 17, 318.

‡ Compt. Rend., 20, 1047. Journ. für Prakt. Chem., 35, 73.

|| Arch. d. Sci. Phys. et Nat., 8, 271.

A.

96.356
96.345
96.362

Mean, 96.3543, ± .0033

B.

96.356
96.452

Mean, 96.354, ± .0013

C.

96.358
96.363

Mean, 96.3605, ± .0017

D.

96.346
96.384
96.361
96.377

Mean, 96.367, ± .0057

Dumas* employed barium chloride prepared from pure barium nitrate, and took the extra precaution of fusing the salt at a red heat in a current of dry hydrochloric acid gas. Three series of experiments upon three samples of chloride gave the following results:

Series A.

1.7585 grm. $BaCl_2$	1.826 grm. Ag.	Ratio, 96.303
3.842 "	3.988 "	96.339
2.1585 "	2.2405 "	96.340
4.0162 "	4.168 "	96.358
		Mean, 96.3325, ± .0068

* Ann. Chem. Pharm., 113, 22. 1860. Ann. Chim. Phys., (3,) 55, 129.

Series B.

1.6625 grm. $BaCl_2$ =	1.727 grm. Ag.	Ratio,	96.265
2.4987 "	2.5946 "		96.304
3.4468 "	3.579 "		96.306
4.0822 "	4.2395 "		96.290
4.2062 "	4.3683 "		96.289
4.4564 "	4.629 "		96.271
8.6975 "	9.031 "		96.307
		Mean,	96.2902, ± .0043

Series C.

2.2957 grm. $BaCl_2$ =	2.3835 grm. Ag.	Ratio,	96.316
4.1372 "	4.293 "		96.371
4.2662 "	4.430 "		96.303
4.4764 "	4.647 "		96.329
5.6397 "	5.852 "		96.372
		Mean,	96.33382, ± .0096

We have now eight series of experiments upon this ratio, representing thirty distinct estimations. Combining, we get a general mean as follows:

Pelouze	96.4573, ± .0036
Marignac, A	96.3543, ± .0033
" B	96.3540, ± .0013
" C	96.3605, ± .0017
" D	96.3670, ± .0057
Dumas, A	96.3325, ± .0068
" B	96.2902, ± .0043
" C	96.3382, ± .0096
General mean	96.3596, ± .0009

The ratio between silver and crystallized barium chloride has also been fixed by Marignac.* The usual method was employed, and two series of experiments were made; in the second of which the water of crystallization was determined previous to the estimation. Five grammes of chloride were taken in each determination. The following quantities of $BaCl_2.2H_2O$ correspond to 100 parts of silver:

* Journ. f. Prakt. Chem., 74, 212. 1858.

A.	B.
113.109	113.135
113.135	113.122
113.097	113.060
Mean, 113.114, ± .0074	Mean, 113.106, ± .0154

The general mean from both series is 113.113, ± .0067.

The direct ratio between the chlorides of silver and barium was early established both by Berzelius* and Turner.† Berzelius found that 100 parts of dry barium chloride gave of silver chloride:

138.06
138.08

Mean, 138.07, ± .007

Turner made five experiments, with the following results:

137.45
137.54
137.70
137.62
137.64

Of these, Turner regards the fourth and fifth as the most exact. These give a mean of 137.63, ± .007, while the other three are in mean 137.563, ± .049. Combining Berzelius' figures with those of Turner, we get as follows:

Berzelius	138.07, ± .007
Turner, 1, 2, 3	137.563, ± .049
" 4, 5	137.63, ± .007
General mean	137.841, ± .0047

Incidentally to some of his other work Marignac‡ determined the percentage of water in crystallized barium chloride. Two sets of three experiments each were made, the first upon five grammes and the second upon ten grammes of salt. The following are the percentages obtained:

* Poggend. Annal., 8, 177.
† Phil. Trans., 1829, 291.
‡ Journ. f. Prakt. Chem., 74, 212. 1858.

A.	B.
14.790	14.80
14.796	14.81
14.800	14.80
Mean, 14.795, ± .0019	Mean, 14.803, ± .002

General mean of both series, 14.799, ± .0014

The ratio between barium nitrate and barium sulphate has been determined only by Turner.* According to his experiments 100 parts of sulphate correspond to the following quantities of nitrate:

112.060
111.990
112.035

Mean, 112.028, ± .014

For the similar ratio between the sulphate and the chloride there are experiments by Turner, Berzelius, Struve, and Marignac. Turner† found that 100 parts of chloride ignited with sulphuric acid gave 112.19 parts of sulphate. By the common method of precipitation and filtration a lower figure was obtained, because of the slight solubility of the sulphate. This point bears directly upon many other atomic weight determinations.

Berzelius,‡ treating barium chloride with sulphuric acid, obtained the following results in $BaSO_4$ for 100 parts of $BaCl_2$:

112.17
112.18

Mean, 112.175, ± .0034

Struve,|| in two experiments, found:

112.0912
112.0964

Mean, 112.0938, ± .0018

* Phil. Trans., 1833, 538.
† Phil. Trans., 1829, 291.
‡ Poggend. Annal., 8, 177.
|| Ann. Chem. Pharm., 80, 204. 1851.

Marignac's* three results are as follows:

8.520 grm. $BaCl_2$ gave	9.543	$BaSO_4$.	Ratio,	112.007	
8.519	"	9.544	"	112.032	
8.520	"	9.542	"	111.995	
			Mean,	112.011,	± .0071

Rejecting Turner's single result as unimportant, we may combine the other series:

Berzelius	112.175,	± .0034
Struve	112.0938,	± .0018
Marignac	112.011,	± .0071
General mean	112.106,	± .0015

The data from which we are to calculate the atomic weight of barium may now be tabulated as follows:

(1.) $Ag_2 : BaCl_2 :: 100 : 96.3596$, ± .0009
(2.) $Ag_2 : BaCl_2.2H_2O :: 100 : 113.113$, ± .0067
(3.) $BaCl_2 : 2AgCl :: 100 : 137.841$, ± .0047
(4.) Per cent. of H_2O in $BaCl_2.2H_2O$, 14.799, ± .0014
(5.) $BaSO_4 : BaN_2O_6 :: 112.028$, ± .014
(6.) $BaCl_2 : BaSO_4 :: 100 : 112.106$, ± .0015

From these ratios, with the aid of the atomic weights already established, we can immediately calculate four independent values for the molecular weight of $BaCl_2$:

From (1)	$BaCl_2$	= 207.510, ± .019
From (2)	"	= 207.662, ± .027
From (3)	"	= 207.536, ± .017
From (4)	"	= 206.837, ± .045
General mean	"	= 207.505, ± .011

We have here an interesting example of the compensation of constant errors. Ratios (2) and (4) both represent work done by Marignac upon barium chloride containing water of crystallization. If now, as is not improbable, the salt contained a trifling excess of water, the molecular weight of barium chloride as calculated from (2) would come out too high, while on the other hand the result from ratio (4) would err in the opposite direction. In point of fact, the

* Journ. f. Prakt. Chem., 74, 212. 1858.

two results in the present calculation nearly compensate each other, and, on account of their relatively high probable errors, they exert but an unimportant influence upon the general mean.

In conclusion, we have three independent values for the atomic weight of barium:

From mol. wt. of $BaCl_2$	Ba	$= 136.765, \pm .031$
From ratio (5)	"	$= 136.795, \pm .364$
From ratio (6)	"	$= 136.595, \pm .309$
General mean	"	$= 136.763, \pm .031$

If $O = 16$, then $Ba = 137.007$. In other words, the ratio between oxygen and barium is almost an exact ratio between two whole numbers.

In the above discussion it will at once be noticed that the second and third values for Ba have very high probable errors, and that they therefore exert almost no influence upon the general mean. This fact by no means renders them worthless however, for, at the lowest estimate, they are useful in confirmation of the better determinations. It is also highly probable that the method of discussion, rigidly carried out, does not do them absolute justice.

STRONTIUM.

The ratios which fix the atomic weight of strontium resemble in general terms those relating to barium, only they are fewer in number and represent a comparatively small amount of work. The early experiments of Stromeyer,* who measured the volume of CO_2 evolved from a known weight of strontium carbonate, are hardly available for the present discussion. So also we may exclude the determination by Salvétat,† who neglected to publish sufficient details.

Taking the ratio between strontium chloride and silver first in order, we have series of figures by Pelouze and by Dumas. Pelouze‡ employed the volumetric method already described under barium, and in two experiments obtained the subjoined results. In another column I append the ratio between $SrCl_2$ and 100 parts of silver:

1.480 grm. $SrCl_2$ =	2.014 grm. Ag.	73.486
2.210 "	3.008 "	73.471
		Mean, 73.4781, ± .0050

Dumas,‖ by the same general method, made sets of experiments with three samples of chloride which had previously been fused in a current of dry hydrochloric acid. His results, expressed in the usual way, are as follows:

Series A.

3.137 grm. $SrCl_2$ =	4.280 grm. Ag.	Ratio, 73.2944
1.982 "	2.705 "	73.2717
3.041 "	4.142 "	73.4186
3.099 "	4.219 "	73.4534
		Mean, 73.3595, ± .0303

* Schweigg. Journ., 19, 228. 1816.
† Compt. Rend., 17, 318. 1843.
‡ Compt. Rend., 20, 1047. 1845.
‖ Ann. Chim. Phys., (3.) 55, 29. 1859. Ann. Chem. Pharm., 113, 34.

Series B.

3.356 grm. $SrCl_2$	=	4.574 grm. Ag.		Ratio,	73.3713
6.3645	"	8.667	"		73.4327
7.131	"	9.712	"		73.4246
				Mean,	73.4095, ± .0130

Series C.

7.213 grm. $SrCl_2$	=	9.811 grm. Ag.		Ratio,	73.5195
2.206	"	3.006	"		73.3866
4.268	"	5.816	"		73.5529
4.018	"	5.477	"		73.3613
				Mean,	73.4551, ± .0321

Combining, we have:

Pelouze	73.4781, ± .0050
Dumas, A	73.3595, ± .0303
" B	73.4095, ± .0130
" C	73.4551, ± .0321
General mean	73.4655, ± .0046

The foregoing figures apply to anhydrous strontium chloride. The ratio between silver and the crystallized salt, $SrCl_2.6H_2O$, has also been determined in two series of experiments by Marignac.* Five grammes of salt were used in each estimation, and, in the second series, the percentage of water was first determined. The quantities of the salt corresponding to 100 parts of silver are given in the last column:

Series A.

5 grm. $SrCl_2.6H_2O$	=	4.0515 grm. Ag.		123.411
"	"	4.0495	"	123.472
"	"	4.0505	"	123.442
			Mean,	123.442, ± .012

Series B.

5 grm. $SrCl_2.6H_2O$	=	4.0490 grm. Ag.		123.487
"	"	4.0500	"	123.457
"	"	4.0490	"	123.487
			Mean,	123.477, ± .007

General mean of both series, 123.470, ± .006

* Journ. Prakt. Chem., 74, 216. 1858.

In the same paper Marignac gives two sets of determinations of the percentage of water in crystallized strontium chloride. The first set, corresponding to "B" above, comes out thus:

40.556
40.568
40.566

Mean, 40.563, $\pm$ .0024

In the second set ten grammes of salt were taken at a time, and the following percentages were found:

40.58
40.59
40.58

Mean, 40.583, $\pm$ .0020

General mean, from both series, 40.575, $\pm$ .0015

The chloride used in the series of estimations last given was subsequently employed for ascertaining the ratio between it and the sulphate. Converted directly into sulphate, 100 parts of chloride yield the quantities given in the third column:

5.942 grm. $SrCl_2$ gave	6.887 grm. $SrSO_4$.	115.932
5.941 "	6.8855 "	115.949
5.942 "	6.884 "	115.927
		Mean, 115.936, $\pm$ .004

Now, to sum up the ratios and calculate the atomic weight of strontium.

(1.) $Ag : SrCl_2 :: 100 : 73.4655$, $\pm$ .0046
(2.) $Ag : SrCl_2.6H_2O :: 100 : 123.470$, $\pm$ .006
(3.) Per cent. of H_2O in $SrCl_2.6H_2O$, 40.575, $\pm$ .0015
(4.) $SrCl_2 : SrSO_4 :: 100 : 115.936$, $\pm$ .004

We now have the molecular weight of $SrCl_2$, as follows:

From (1)	$SrCl_2$	= 158.208, $\pm$ .017
From (2)	"	= 158.113, $\pm$ .034
From (3)	"	= 157.852, $\pm$ .032
General mean	"	= 158.124, $\pm$ .014

And for the atomic weight of strontium itself we have two values, as follows:

1. From mol. wt. of $SrCl_2$	Sr	$= 87.384, \pm .032$
2. From (4)	"	$= 86.765, \pm .244$
General mean	"	$= 87.374, \pm .032$

If O = 16, then Sr = 87.575.

CALCIUM.

For determining the atomic weight of calcium we have sets of experiments by Berzelius, Erdmann and Marchand, and Dumas. Salvétat* also has published an estimation, but without the details necessary to enable us to make use of his results. I also find a reference† to some work of Marignac; which, however, seems to have been of but little importance. The earlier work of Berzelius was very inexact as regards calcium, and it is not until we come down to the year 1842 that we find any material of decided value.

The most important factor in our present discussion is the composition of calcium carbonate, as worked out by Dumas and by Erdmann and Marchand.

In 1842 Dumas‡ made three ignitions of Iceland spar, and determined the percentages of carbon dioxide driven off and of lime remaining. The impurities of the material were also determined, the correction for them applied, and the weighings reduced to a vacuum standard. The percentage of lime came out as follows:

56.12
56.04
56.06

Mean, 56.073, ± .016

* Compt. Rend., 17, 318. 1843.
† See Oudeman's monograph, p. 51.
‡ Compt. Rend., 14, 537. 1842.

About this same time Erdmann and Marchand* began their researches upon the same subject. Two ignitions of spar, containing .04 per cent. of impurity, gave respectively 56.09 and 56.18 per cent. of residue; but these results are not exact enough for us to consider further. Four other results obtained with artificial calcium carbonate are more noteworthy. The carbonate was precipitated from a solution of pure calcium chloride by ammonium carbonate, was washed thoroughly with hot water, and dried at a temperature of 180°. With this preparation the following residues of lime were obtained:

56.03
55.98
56.00
55.99

Mean, 56.00, ± .007

It was subsequently shown by Berzelius that calcium carbonate prepared by this method retains traces of water even at 200°, and that minute quantities of chloride are also held by it. These sources of error are, however, in opposite directions, since one would tend to diminish and the other to increase the weight of residue.

In the same paper there are also two direct estimations of carbonic acid in pure Iceland spar, which correspond to the following percentages of lime:

56.00
56.02

Mean, 56.01, ± .007

In a still later paper† the same investigators give another series of results based upon the ignition of Iceland spar. The impurities were carefully estimated, and the percentages of lime are suitably corrected:

* Journ. für Prakt. Chem., 26, 472. 1842.
† Journ. für Prakt. Chem., 31, 269. 1844.

4.2134 grm. $CaCO_3$ gave	2.3594 grm. CaO.		55.997 per cent.
15.1385 "	8.4810	"	56.022 "
23.5503 "	13.1958	"	56.031 "
23.6390 "	13.2456	"	56.032 "
42.0295 "	23.5533	"	56.044 "
49.7007 "	27.8536	"	56.042 "
		Mean,	56.028, ± .0047

Six years later Erdmann and Marchand* published one more result upon the ignition of calcium carbonate. They found that the compound began giving off carbon dioxide below the temperature at which their previous samples had been dried, or about 200°, and that, on the other hand, traces of the dioxide were retained by the lime after ignition. These two errors do not compensate each other, since both tend to raise the percentage of lime. In the one experiment now under consideration these errors were accurately estimated, and the needful corrections were applied to the final result. The percentage of residual lime in this case came out 55.998. This agrees tolerably well with the figures found in the direct estimation of carbonic acid, and, if combined with those two, gives a mean for all three of 56.006, ± .0043.

Combining all these series we get the following result:

Dumas	56.073,	± .016
Erdmann and Marchand	56.006,	± .007
" "	56.028,	± .0047
" "	56.006,	± .0043
General mean	56.0198,	± .0029

For reasons given above this mean is probably vitiated by a slight constant error, which makes the figure a trifle too high.

In the earliest of three papers by Erdmann and Marchand there is also given a series of determinations of the ratio between calcium carbonate and sulphate. Pure Iceland

* Journ. für Prakt. Chem., 50, 237. 1850.

spar was carefully converted into calcium sulphate, and the gain in weight noted. One hundred parts of spar gave of sulphate:

136.07
136.06
136.02
136.06

Mean, 136.0525, ± .0071

In 1843 the atomic weight of calcium was redetermined by Berzelius,* who investigated the ratio between lime and calcium sulphate. The calcium was first precipitated from a pure solution of nitrate by means of ammonium carbonate, and the thoroughly washed precipitate was dried and strongly ignited in order to obtain lime wholly free from extraneous matter. This lime was then, with suitable precautions, treated with sulphuric acid, and the resulting sulphate was weighed. Correction was applied for the trace of solid impurity contained in the acid, but not for the weighing in air. The figures in the last column represent the percentage of weight gained by the lime upon conversion into sulphate:

1.80425 grm. CaO	gained	2.56735	grm.	142.295
2.50400	"	3.57050	"	142.592
3.90000	"	5.55140	"	142.343
3.04250	"	4.32650	"	142.202
3.45900	"	4.93140	"	142.567

Mean, 142.3998, ± .0518

Last of all we have the ratio between calcium chloride and silver, as determined by Dumas.† Pure calcium chloride was first ignited in a stream of dry hydrochloric acid, and the solution of this salt was afterwards titrated with a silver solution in the usual way. The $CaCl_2$ proportional to 100 parts of Ag is given in a third column:

* Journ. für Prakt. Chem., 31, 263. Ann. Chem. Pharm., 46, 241.
† Ann. Chim. Phys., (3,) 55, 129. 1859. Ann. Chem. Pharm., 113, 34.

2.738 grm. $CaCl_2$ =	5.309 grm. Ag.		51.573
2.436 "	4.731 "		51.490
1.859 "	3.617 "		51.396
2.771 "	5.3885 "		51.424
2.240 "	4.3585 "		51.394
		Mean,	51.4554, ± .0230

We have now four ratios to calculate from, as follows:

(1.) Per cent. of CaO in $CaCO_3$, 56.0198, ± .0029
(2.) CaO : SO_3 : : 100 : 142.3998, ± .0518
(3.) $CaCO_3$: $CaSO_4$: : 100 : 136.0525, ± .0071
(4.) Ag : $CaCl_2$: : 100 : 51.4554, ± .0230

These give us the subjoined values for calcium:

From (1) .... Ca	= 39.955, ± .011
From (2) .... "	= 40.139, ± .023
From (3) .... "	= 39.925, ± .068
From (4) .... "	= 40.069, ± .058
General mean .... "	= 39.990, ± .010

If O = 16, then Ca = 40.082.

A glance at the above figures will show that, if, as is probable, the value deduced from the composition of calcium carbonate is a trifle too high, the general mean must be too high also. It is, therefore, interesting to see what result the very latest of Erdmann and Marchand's experiments will lead to. They found, after taking every precaution, in a single experiment that calcium carbonate yielded 55.998 per cent. of lime. From this we get Ca = 39.905; or, if O = 16, Ca = 39.997. It is possible, then, that "Prout's law" may hold good for calcium.

LEAD.

For the atomic weight of lead we have to consider experiments made upon the oxide, chloride, nitrate, and sulphate. The researches of Berzelius upon the carbonate and various organic salts need not now be considered, nor is it worth while to take into account any work of his done before the year 1818. The results obtained by Döbereiner* and by Longchamp† are also without special present value.

For the exact composition of lead oxide we have to depend upon the researches of Berzelius. His experiments were made at different times through quite a number of years; but were finally summed up in the last edition of his famous "Lehrbuch."‡ In general terms his method of experiment was very simple. Perfectly pure lead oxide was heated in a current of hydrogen, and the reduced metal weighed. From his weighings I have calculated the percentages of lead thus found and given them in a third column:

		Earlier Results.		
8.045 grm. PbO	gave	7.4675 grm. Pb.		92.8217 per cent.
14.183	"	13.165	"	92.8224 "
10.8645	"	10.084	"	92.8160 "
13.1465	"	12.2045	"	92.8346 "
21.9425	"	20.3695	"	92.8313 "
11.159	"	10.359	"	92.8309 "
		Latest.		
6.6155	"	6.141	"	92.8275 "
14.487	"	13.448	"	92.8280 "
14.626	"	13.5775	"	92.8313 "
				Mean, 92.8271, $\pm$ .0013

For the synthesis of lead sulphate we have data by Berzelius, Turner, and Stas. Berzelius,‖ whose experiments

* Schweig. Journ., 17, 241. 1816.
† Ann. Chim. Phys., 34, 105. 1827.
‡ Bd. 3, s. 1218.
‖ Lehrbuch, 5th Ed., 3, 1187.

were intended rather to fix the atomic weight of sulphur, dissolved in each estimation ten grammes of pure lead in nitric acid, then treated the resulting nitrate with sulphuric acid, brought the sulphate thus formed to dryness, and weighed. One hundred parts of metal yield of $PbSO_4$:

146.380
146.400
146.440
146.458

Mean, 146.419, ± .012

Turner,* in three similar experiments, found as follows:

146.430
146.398
146.375

Mean, 146.401, ± .011

In these results of Turner's *absolute* weights are implied. The results of Stas' syntheses,† effected after the same general method, but with variations in details, are as follows. Corrections for weighing in air were applied:

146.443
146.427
146.419
146.432
146.421
146.423

Mean, 146.4275, ± .0024

Combining, we get the subjoined result:

Berzelius	146.419, ± .012
Turner	146.401, ± .011
Stas	146.4275, ± .0024
General mean	146.4262, ± .0023

Turner, in the same paper, also gives a series of syntheses of lead sulphate, in which he starts from the oxide instead

* Phil. Trans., 1833, 527–538.
† Aronstein's Translation, 333.

of from the metal. One hundred parts of PbO, upon conversion into $PbSO_4$, gained weight as follows:

35.84
35.71
35.84
35.75
35.79
35.78
35.92

Mean, 35.804, $\pm$ .018

These figures are not wholly reliable. Numbers one, two, and three represent lead oxide contaminated with traces of nitrate. The oxide of four, five, and six contained traces of minium. Number seven was free from these sources of error, and, therefore, deserves more consideration. The series as a whole undoubtedly gives too low a figure; and this error would tend to slightly raise the atomic weight of lead.

Still a third series by Turner establishes the ratio between the nitrate and the sulphate; a known weight of the former being in each experiment converted into the latter. One hundred parts of sulphate represent of nitrate:

109.312
109.310
109.300

Mean, 109.307, $\pm$ .002

In all these experiments by Turner the necessary corrections were made for weighing in air.

For the ratio between lead chloride and silver we have a series of results by Marignac and one experiment by Dumas. There are also unavailable data by Turner and by Berzelius.

Marignac,* applying the method used in his researches upon barium and strontium, and working with lead chloride which had been dried at 200°, obtained these results.

* Journ. für Prakt. Chem., 74, 218. 1858.

The third column gives the ratio between $PbCl_2$ and 100 parts of Ag:

4.9975	grm. $PbCl_2$ =	3.8810	grm. Ag.		128.768
4.9980	"	3.8835	"		128.698
5.0000	"	3.8835	"		128.750
5.0000	"	3.8860	"		128.667
				Mean,	128.721, ± .016

Dumas,* in his investigations, found that lead chloride retains traces of water even at 250°, and is sometimes also contaminated with oxychloride. In one estimation 8.700 grammes $PbCl_2$ saturated 6.750 of Ag. The chloride contained .009 of impurity: hence, correcting, Ag : $PbCl_2$: : 100 : 128.750. If we assign this figure equal weight with those of Marignac, we get as the mean of all, 128.7266, ± .013. The sources of error indicated by Dumas, if they are really involved in this mean, would tend slightly to raise the atomic weight of lead.

The synthesis of lead nitrate, as carried out by Stas,† gives excellent results. Two series of experiments were made, with from 103 to 250 grammes of lead in each determination. The metal was dissolved in nitric acid, the solution evaporated to dryness with extreme care, and the nitrate weighed. All weighings were reduced to the vacuum standard. In series A the lead nitrate was dried in an air current at a temperature of about 155°. In series B the drying was effected in vacuo. 100 of lead yield of nitrate:

A.

159.973
159.975
159.982
159.975
159.968
159.973

Mean, 159.9743, ± .0012

* Ann. Chem. Pharm., 113, 35. 1860.
† Aronstein's Translation, 326.

B.

159.970
159.964
159.959
159.965

Mean, 159.9645, ± .0015

Mean from both series, 159.9704, ± .0010

There still remain to be noticed two sets of experiments upon lead nitrate, which were originally intended to establish the atomic weight of nitrogen. Lead nitrate was carefully ignited and the residual oxide weighed. The first series, bearing Svanberg's name,* gives simply the percentage of oxide found, as follows:

67.4030
67.4036
67.4043
67.3956

Mean, 67.4016, ± .0014

The second series is by Anderson,† and gives the weighings upon which the percentages rest. The latter come out thus:

5.19485 grm. PbN_2O_6 gave	3.5017 grm. PbO.	67.4071 per cent.
9.7244 "	6.5546 "	67.4037 "
9.2181 "	6.2134 "	67.4044 "
9.6530 "	6.5057 "	67.3957 "

Mean, 67.4027, ± .0016

It will at once be seen that these series are identical; the discordance between the first figures of the two being undoubtedly due to some misprint in the weighings of the Anderson set. How it happens that the same work has been published by two separate authors I will not attempt to explain; neither will I undertake to determine which of the two is really entitled to credit.

* Journ. für Prakt. Chem., 27, 381. 1842.
† Ann. Chim. Phys., (3,) 9, 254. 1843.

We have now seven ratios upon which to base our computations:

(1.) Per cent. of Pb in PbO, 92.8271, ± .0013
(2.) Per cent. of PbO in PbN_2O_6, 67.4016, ± .0014
(3.) Pb : $PbSO_4$: : 100 : 146.4262, ± .0023
(4.) PbO : $PbSO_4$: : 100 : 135.804, ± .018
(5.) $PbSO_4$: PbN_2O_6 : : 100 : 109.307, ± .002
(6.) Pb : PbN_2O_6 : : 100 : 159.9704, ± .0010
(7.) Ag : $PbCl_2$: : 100 : 128.7266, ± .013

Discussing these separately, we get an equal number of values for the atomic weight of lead:

From (1)	Pb		206.587, ± .059
" (2)	"	=	207.046, ± .041
" (3)	"	=	206.435, ± .041
" (4)	"	=	207.131, ± .118
" (5)	"	=	204.803, ± .329
" (6)	"	=	206.454, ± .037
" (7)	"	=	206.473, ± .042
General mean	"	=	206.604, ± .019

If O = 16, this becomes Pb = 207.079.

In the above discussion are included several values which diverge widely from this general mean, and which, for other reasons, are probably erroneous. Although but one of these carries much weight, it is as well to exclude them, and to base our computations upon the others. If, now, we reject the second, fourth, and fifth values, we get for the atomic weight of lead, Pb = 206.471, ± .021. If O = 16, this becomes Pb = 206.946.

From the synthesis of the nitrate Stas found 206.918, and from the sulphate, 206.934. The agreement of these values with our own general mean is certainly very close.

FLUORINE.

The atomic weight of fluorine has been determined only by one general method, namely, by the conversion of fluorides into sulphates. Excluding the early results of Davy,* we have only to consider the experiments of Berzelius, Louyet, Dumas, and DeLuca, with reference to the fluorides of calcium, sodium, potassium, barium, and lead.

The ratio between calcium fluoride and sulphate has been determined by the four investigators above named, and by one general process. The fluoride is treated with strong sulphuric acid, the resulting sulphate is ignited, and the product weighed. In order to ensure complete transformation special precautions are necessary; such, for instance, as repeated treatment with sulphuric acid, and so on. For details like these the original papers must be consulted.

The first experiments in chronological order are those of Berzelius,† who operated upon an artificial calcium fluoride. He found, in three experiments, for one part of fluoride the following of sulphate:

1.749
1.750
1.751

Mean, 1.750, ± .0004

Louyet's researches‡ were much more elaborate than the foregoing. He began with a remarkably concordant series of results upon fluor spar, in which one gramme of the fluoride yielded from 1.734 to 1.737 of sulphate. At first he regarded these as accurate, but he soon found that particles of spar had been coated with sulphate, and had therefore escaped action. In the following series this source of error was guarded against.

* Phil. Trans., 1814, 64.
† Poggend. Annal., 8, 1. 1826.
‡ Ann. Chim. Phys., (3,) 25, 300. 1849.

Starting with fluor spar, Louyet found of sulphate as follows:

1.742
1.744
1.745
1.744
1.7435
1.7435

Mean, 1.7437, ± .0003

A second series, upon artificial fluoride, gave:

1.743
1.741
1.741

Mean, 1.7417, ± .0004

Dumas* published but one result for calcium fluoride. .495 grm. gave .864 grm. sulphate, the ratio being 1 : 1.7455.

De Luca† worked with a very pure fluor spar, and published the following results. The ratio between $CaSO_4$ and one gramme of CaF_2 is given in the third column:

.9305 grm. CaF_2 gave		1.630 grm. $CaSO_4$.		1.7518
.836	"	1.459	"	1.7452
.502	"	.8755	"	1.7440
.3985	"	.6945	"	1.7428

If we include Dumas' single result with these, we get a mean of 1.7459, ± .0011.

Upon combining all these series, we get as follows:

Berzelius	1.7500, ± .0004
Louyet, 1st series	1.7437, ± .0003
" 2d "	1.7417, ± .0004
De Luca and Dumas	1.7459, ± .0011
General mean	1.74493, ± .0002

For the ratio between the two sodium salts we have experiments by Dumas and by Louyet.‡ According to Louyet one gramme of NaF gives of Na_2SO_4:

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* Ann. Chem. Pharm., 113, 28. 1860.

† Compt. Rend., 51, 299. 1860.

‡ See the papers already quoted.

1.686
1.683
1.685

Mean, 1.6847, ± .0006

The weighings published by Dumas are as follows:

.777 grm. NaF give	1.312 grm. Na_2SO_4.	Ratio,	1.689
1.737 "	2.930 "	"	1.687
		Mean,	1.688, ± .0007

The general mean of both series is 1.6863, ± .0004.

Dumas also gives experiments upon potassium fluoride. The quantity of sulphate formed from one gramme of fluoride is given in the last column:

1.483 grm. KF give	2.225 grm. K_2SO_4.	1.5002
1.309 "	1.961 "	1.4981
		Mean, 1.4991, ± .0007

The ratios for the fluorides of lead and of barium are due entirely to Louyet. One gramme BaF_2 gave of $BaSO_4$:

1.332
1.331
1.330

Mean, 1.331, ± .0004

With the lead fluoride a new method of treatment was adopted. The salt was fused, powdered, dissolved in nitric acid, and precipitated by dilute sulphuric acid. The evaporation of the fluid and the ignition of the sulphate was then effected without transfer. Five grammes of fluoride were taken in each operation, yielding of sulphate:

6.179
6.178
6.178

Mean, 6.1783, ± .0002

We now have five ratios to calculate from, as follows:

(1.) $CaF_2 : CaSO_4 :: 1.0 : 1.74493, \pm .0002$
(2.) $NaF : Na_2SO_4 :: 1.0 : 1.6863, \pm .0004$
(3.) $KF : K_2SO_4 :: 1.0 : 1.4991, \pm .0007$
(4.) $BaF_2 : BaSO_4 :: 1.0 : 1.3310, \pm .0004$
(5.) $PbF_2 : PbSO_4 :: 5.0 : 6.1783, \pm .0002$

From these we get five values for F:

From (1)------------------	F = 18.926, ± .009
" (2)------------------	" = 19.050, ± .014
" (3)------------------	" = 18.975, ± .032
" (4)------------------	" = 18.993, ± .033
" (5)------------------	" = 19.092, ± .016
General mean--------	" = 18.984, ± .0065

If O = 16, this becomes 19.027.

Before leaving the subject of fluorine we must notice two possible sources of error beyond the always to be considered one of impurities in the materials employed. First, an incomplete conversion of a fluoride into a sulphate would lead to results tending to raise the atomic weight of fluorine. On the other hand, the value for fluorine which has most weight is that derived from calcium fluoride. But it was shown under calcium that the atomic weight determined for that metal was probably a trifle too high. This error, introduced into our fluorine calculations, tends to lower our final results. These two errors, then, if they really exist, will, in part at least, compensate each other.

PHOSPHORUS.

The material from which we are to calculate the atomic weight of phosphorus is by no means abundant. Berzelius, in his Lehrbuch,* adduces only his own experiments upon the precipitation of gold by phosphorus, and ignores all the earlier work relating to the composition of the phosphates. These experiments we will consider with reference to gold.

Pelouze,† in a single titration of phosphorus trichloride with a standard solution of silver, obtained a wholly erroneous result; and Jacquelain,‡ in his similar experiments, did even worse. Schrötter's criticism upon Jacquelain sufficiently disposes of the latter.||

There are, in short, but two investigations upon the atomic weight of phosphorus which have any value for present purposes, namely, the researches of Schrötter and of Dumas. These chemists worked with different materials and by different methods, and yet obtained beautifully concordant results.

Schrötter§ burned pure amorphous phosphorus in dry oxygen, and weighed the pentoxide thus formed. One gramme of P yielded P_2O_5 in the following proportions:

2.28909
2.28783
2.29300
2.28831
2.29040
2.28788
2.28848
2.28856
2.28959
2.28872

Mean, 2.289186, ± .00033

Hence P = 30.9562, ± .0074.

* 5th Ed., 1188.
† Compt. Rend., 20, 1047.
‡ Compt. Rend., 33, 693.
|| Journ. für Prakt. Chem., 57, 315.
§ Journ. für Prakt. Chem., 53, 435. 1851.

Dumas* prepared pure phosphorus trichloride by the action of dry chlorine upon red phosphorus. The portion used in his experiments boiled between 76° and 78°. This was titrated with a standard solution of silver in the usual manner. Dumas publishes weights, from which I calculate the figures given in the third column, representing the quantity of trichloride proportional to 100 parts of silver:

1.787 grm. PCl_3	= 4.208 grm. Ag.	42.4667
1.466 "	3.454 "	42.4435
2.056 "	4.844 "	42.4443
2.925 "	6.890 "	42.4528
3.220 "	7.582 "	42.4690
		Mean, 42.4553, ± .0036

Hence P = 31.0314, ± .0467.

Now, combining these two values, we have:

By Schrötter	P = 30.9562, ± .0074
By Dumas	" = 31.0314, ± .0467
General mean	" = 30.9580, ± .0073

If O = 16, this becomes 31.0292.

The fact here noticeable, that Dumas' figures give a value for P slightly higher than that deduced from those of Schrötter, may be accounted for upon the supposition that the phosphorus trichloride contained traces of oxychloride. Such an impurity would tend to raise the apparent atomic weight of phosphorus, and its occurrence is by no means improbable.

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* Ann. Chem. Pharm., 113, 29. 1860.

BORON.

The atomic weight of this element has been determined by Berzelius and by Laurent, and calculated by Dumas from some experiments by Deville.

Berzelius* based his determination upon three concordant estimations of the percentage of water in borax. Laurent† made use of two similar estimations, and all five may be properly put in one series, thus:

47.10	Berzelius.
47.10	
47.10	
47.15	Laurent.
47.20	

Mean, 47.13, ± .013

Hence B = 10.943, ± .023.

Dumas'‡ calculations were based on Deville's analyses of the chloride and bromide of boron, which give the ratios between AgCl and BCl_3, and between AgBr and BBr_3. Reducing the weighings to a common standard, 100 parts of silver chloride correspond to the quantities of boron trichloride given in the third column:

.6763 grm. BCl_3	2.447 grm. AgCl.	27.303
.923 "	3.395 "	27.187

Mean, 27.245, ± .059

Hence B = 10.808, ± .174.

With the bromide, 2.446 BBr_3 gave 5.496 AgBr. If we assign this experiment equal weight with one in the chloride series, and include the probable error of Br, B = 10.964, ± .364.

The three values combine as follows:

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* Poggend. Annal., 8, 1. 1826.

† Journ. für Prakt. Chem., 47, 415. 1849.

‡ Ann. Chem. Pharm., 113, 31. 1860.

From borax	B =	10.943, ± .023
From BCl_3	" =	10.808, ± .174
From BBr_3	" =	10.964, ± .364
General mean	" =	10.941, ± .023

If O = 16, B = 10.966.

Further investigation of the atomic weight of boron is evidently desirable.

SILICON.

Although Berzelius* attempted to ascertain the atomic weight of silicon, first by converting pure Si into SiO_2, and later from the analysis of $BaSiF_6$, his results were not satisfactory. We need only consider the estimations of Pelouze, Schiel, and Dumas.

Pelouze,† experimenting upon silicon tetrachloride, employed his usual method of titration with a solution containing a known weight of silver. One hundred parts of Ag gave the following equivalencies of $SiCl_4$:

39.4325
39.4570

Mean, 39.4447, ± .0083

Hence Si = 28.408.

Essentially the same method was adopted by Dumas.‡ Pure $SiCl_4$ was weighed in a sealed glass bulb, then decomposed by water, and titrated. The results for 100 Ag are given in the third column:

2.899 grm. $SiCl_4$ =	7.3558 grm. Ag.	39.411
1.242 "	3.154 "	39.379
3.221 "	8.1875 "	39.340
	Mean,	39.377, ± .014

Hence Si = 28.117.

* Lehrbuch, 5 Aufl., 3, 1200.
† Compt. Rend., 20, 1047. 1845.
‡ Ann. Chem. Pharm., 113, 31. 1860.

Dumas and Pelouze's series combine as follows:

Pelouze	39.4447, ± .0083
Dumas	39.377, ± .014
General mean	39.4265, ± .0071

Hence $SiCl_4$ = 169.810, ± .034.

Schiel,* also studying the chloride of silicon, decomposed it by ammonia. After warming and long standing it was filtered, and in the filtrate the chlorine was estimated as AgCl. One hundred parts of AgCl correspond to the quantities of $SiCl_4$ given in the last column:

.6738 grm. $SiCl_4$ gave	2.277 grm. AgCl.	29.592
1.3092 "	4.418 "	29.633
	Mean,	29.6125, ± .0138

Hence $SiCl_4$ = 169.437, ± .080, and Si = 27.957.

Combining the values for $SiCl_4$ we have this result:

Pelouze and Dumas $SiCl_4$	= 169.810, ± .034
Schiel "	= 169.437, ± .080
General mean "	= 169.675, ± .031

Hence Si = 28.195, ± .066; or, if O = 16, Si = 28.260.

It will be observed that all of these determinations rest upon the composition of $SiCl_4$, a compound for which it would not be easy to guarantee absolute purity. All the errors likely to occur in the determination of the atomic weight would be plus errors, so that the value deduced above is almost certainly too high.

* Ann. Chem. Pharm., 120, 94.

LITHIUM.

The earlier determinations of the atomic weight of lithium by Arfvedson, Stromeyer, C. G. Gmelin, and Kralovanzky were all erroneous, because of the presence of sodium compounds in the material employed. The results of Berzelius, Hagen, and Hermann were also incorrect, and need no further notice here. The only investigations which we need to consider are those of Mallet, Diehl, Troost, and Stas.

Mallet's experiments* were conducted upon lithium chloride, which had been purified as completely as possible. In two trials the chloride was precipitated by nitrate of silver, which was collected upon a filter and estimated in the ordinary way. The figures in the third column represent the LiCl proportional to 100 parts of AgCl:

7.1885 grm. LiCl gave	24.3086 grm. AgCl.	29.606
8.5947 "	29.0621 "	29.574

In a third experiment the LiCl was titrated with a standard solution of silver. 3.9942 grm. LiCl balanced 10.1702 grm. Ag, equivalent to 13.511 grm. AgCl. Hence 100 AgCl = 29.563 LiCl. Mean of all three experiments, 29.581, ± .0087.

Diehl,† whose paper begins with a good resumé of all the earlier determinations, describes experiments made with lithium carbonate. This salt, which was spectroscopically pure, was dried at 130° before weighing. It was then placed in an apparatus from which the carbon dioxide generated by the action of pure sulphuric acid upon it could be expelled, and the loss of weight determined. From this loss the following percentages of CO_2 in Li_2CO_3 were determined:

59.422
59.404
59.440
59.401

Mean, 59.417, ± .006

* Silliman's Amer. Journal, November, 1856. Chem. Gazette, 15, 7.
† Ann. Chem. Pharm., 121, 93.

Diehl's investigation was quickly followed by a confirmation from Troost.* This chemist, in an earlier paper,† had sought to fix the atomic weight of lithium by an analysis of the sulphate, and had found a value not far from 6.5; thus confirming the results of Berzelius and of Hagen, who had employed the same method. But Diehl showed that the $BaSO_4$ precipitated from Li_2SO_4 always retained traces of Li, which were recognizable by spectral analysis, and which accounted for the error. In the later paper Troost made use of the chloride and the carbonate of lithium, both spectroscopically pure. The carbonate was strongly ignited with pure quartz powder, thus losing carbon dioxide, which loss was easily estimated. The subjoined results were obtained:

.970 grm. Li_2CO_3 lost	.577 grm. CO_2.	59.485 per cent.
1.782 "	1.059 "	59.427 "
	Mean,	59.456, ± .020

This combined with Diehl's mean, 59.417, ± .006, gives a general mean of 59.420, ± .0057.

The lithium chloride employed by Troost was heated in a stream of dry hydrochloric acid gas; of which the excess, after cooling, was expelled by a current of dry air. The salt was weighed in the same tube in which the foregoing operations had been performed, and the chlorine was then estimated as silver chloride. The usual ratio between LiCl and 100 parts of AgCl is given in the third column:

1.309 grm. LiCl gave	4.420 grm. AgCl.	29.615
2.750 "	9.300 "	29.570
	Mean.	29.5925, ± .0145

This combined with Mallet's mean, 29.581, ± .0087, gives a general mean of 59.584, ± .0075.

Finally, we come to the work of Stas,‡ which was exe-

* Zeit. Anal. Chem., 1, 402.

† Annales d. Chim. et d. Phys., 51, 108.

‡ Aronstein's Translation, 279–302.

cuted with his usual wonderful accuracy. In three titrations, in which all the weights were reduced to a vacuum standard, the following quantities of LiCl balanced 100 parts of pure silver:

39.356
39.357
39.361

Mean, 39.358, ± .001

In a second series of experiments, intended for determining the atomic weight of nitrogen, LiCl was converted into $LiNO_3$. The method was that employed for a similar purpose with the chlorides of sodium and of potassium. One hundred parts of LiCl gave of $LiNO_3$:

162.588
162.600
162.598

Mean, 162.5953, ± .0025

We have now the following ratios from which to deduce the atomic weight of lithium:

(1.) AgCl : LiCl : : 100 : 29.584, ± .0075
(2.) Ag : LiCl : : 100 : 39.358, ± .001
(3.) LiCl : $LiNO_3$: : 100 : 162.5953, ± .0025
(4.) Per cent. of CO_2 in Li_2CO_3, 59.420, ± .0057

Hence two values for the molecular weight of LiCl:

From (1)..............LiCl = 42.3187, ± .0039
From (2).............. " = 42.3787, ± .0111

General mean.... " = 42.3720, ± .0037

For lithium itself we get three values:

From molecular weight of LiCl...Li = 7.002, ± .015
From ratio (3).................. " = 7.0287, ± .042
From ratio (4).................. " = 7.0085, ± .008

General mean.......... " = 7.0073, ± .007

If O = 16, then Li = 7.0235. Stas himself gives 7.022 as his determination. Difference, .0015.

RUBIDIUM.

The atomic weight of rubidium has been determined by Bunsen, Piccard, and Godeffroy; but only from analyses of the chloride.

Bunsen,* employing ordinary gravimetric methods, estimated the ratio between AgCl and RbCl. His rubidium chloride was purified by fractional crystallization of the chloroplatinate. He obtained the following results, to which, in a third column, I add the ratio between RbCl and 100 parts of AgCl:

One grm. RbCl gave	1.1873	grm. AgCl.	84.225
"	1.1873	"	84.225
"	1.1850	"	84.388
"	1.1880	"	84.175

Mean, 84.253, ± .031

The work of Piccard† was similar to that of Bunsen. In weighing, the crucible containing the silver chloride was balanced by a precisely similar crucible, in order to avoid the correction for displacement of air. The filter was burned separately from the AgCl, as usual; but the small amount of material adhering to the ash was reckoned as metallic silver. The rubidium chloride was purified by Bunsen's method. The results, expressed according to the foregoing standard, are as follows:

1.1587 grm. RbCl	= 1.372 AgCl	+ .0019 Ag.		84.300
1.4055 "	1.6632 "	.0030 "		84.303
1.001 "	1.1850 "	.0024 "		84.245
1.5141 "	1.7934 "	.0018 "		84.313

Mean, 84.290, ± .0105

Godeffroy,‡ starting with material containing both rubidium and cæsium, separated the two metals by fractional

* Zeit. Anal. Chem., 1, 136. Poggend. Annal., 113, 339. 1861.

† Journ. für Prakt. Chem., 86, 454. 1862. Zeit. Anal. Chem., 1, 518.

‡ Ann. Chem. Pharm., 181, 185. 1876.

crystallization of their alums, and obtained salts of each spectroscopically pure. The nitric acid employed was tested for chlorine and found to be free from that impurity, and the weights used were especially verified. In two of his analyses of RbCl the AgCl was handled by the ordinary process of filtration. In the other two it was washed by decantation, dried, and weighed in a glass dish. The usual ratio is appended in the third column:

1.4055 grm. RbCl gave	1.6665 grm. AgCl.	84.338
1.8096 "	2.1461 "	84.320
2.2473 "	2.665 "	84.326
2.273 "	2.6946 "	84.354
	Mean,	84.3345, $\pm$ .0051

Combining the three series, we get the following result:

Bunsen	84.253, $\pm$ .031	Rb = 85.150
Piccard	84.290, $\pm$ .0105	" = 85.203
Godeffroy	84.3345, $\pm$ .0051	" = 85.263
General mean	84.324, $\pm$ .0045	

Hence Rb = 85.251, $\pm$ .018. If O = 16, Rb = 85.529.

CÆSIUM.

The atomic weight of cæsium, like that of rubidium, has been determined from the analysis of the chloride. The earliest determination, by Bunsen,* was incorrect, because of impurity in the material employed.

In 1863 Johnson and Allen published their results.† Their material was extracted from the lepidolite of Hebron, Maine, and the cæsium was separated from the rubidium as bitartrate. From the pure cæsium bitartrate cæsium chloride was prepared, and in this the chlorine was estimated as

* Zeit. Anal. Chem., 1, 137.

† Amer. Journ. Sci. and Arts, (2,) 35, 94.

silver chloride by the usual gravimetric method. Reducing their results to the convenient standard adopted in preceding chapters, we have, in a third column, the quantities of CsCl equivalent to 100 parts of AgCl:

1.8371 grm. CsCl gave	1.5634 grm. AgCl.		117.507
2.1295	"	1.8111	"	117.580
2.7018	"	2.2992	"	117.511
1.56165	"	1.3302	"	117.399
				Mean, 117.499, ± .025

Shortly after the results of Johnson and Allen appeared a new series of estimations was published by Bunsen.* His cæsium chloride was purified by repeated crystallizations of the chloroplatinate, and the ordinary gravimetric process was employed. The following results represent, respectively, material thrice, four times, and five times purified:

1.3835 grm. CsCl gave		1.1781 grm. AgCl.		Ratio, 117.435
1.3682	"	1.1644	"	117.503
1.2478	"	1.0623	"	117.462
				Mean, 117.467, ± .013

Godeffroy's work† was, in its details of manipulation, sufficiently described under rubidium. In three of the experiments upon cæsium the silver chloride was washed by decantation, and in one it was collected upon a filter. The results are subjoined:

1.5825 grm. CsCl gave		1.351 grm. AgCl.		Ratio, 117.135
1.3487	"	1.1501	"	117.265
1.1880	"	1.0141	"	117.148
1.2309	"	1.051	"	117.107
				Mean, 117.164, ± .023

We may now combine the three series to form a general mean:

* Poggend. Annal., 119, 1. 1863.
† Ann. Chem. Pharm., 181, 185. 1876.

Johnson and Allen	117.499, ± .025	Cs = 132.706
Bunsen	117.467, ± .013	" = 132.661
Godeffroy	117.164, ± .023	" = 132.227
General mean	117.413, ± .010	

Hence Cs = 132.583, ± .024; or, if O = 16, Cs = 132.918.

THALLIUM.

The atomic weight of this interesting metal has been fixed by the researches of Lamy, Werther, Hebberling, and Crookes. Lamy and Hebberling investigated the chloride and sulphate; Werther studied the iodide; Crooke's experiments involved the synthesis of the nitrate. The last mentioned work was so thorough and admirable that the other researches are included here only for the sake of historical completeness.

Lamy* gives the results of one analysis of thallium sulphate and three of thallium chloride. 3.423 grammes Tl_2SO_4 gave 1.578 grm. $BaSO_4$; whence 100 parts of the latter are equivalent to 216.920 of the former. In the thallium chloride the chlorine was estimated as silver chloride. The following results were obtained. In the third column I give the amount of TlCl proportional to 100 parts of AgCl:

3.912 grm. TlCl gave	2.346 grm. AgCl.	166.752
3.000 "	1.8015 "	166.528
3.912 "	2.336 "	167.466
	Mean,	166.915, ± .1905

Hebberling's† work resembles that of Lamy. Reducing his weighings to the standards adopted above, we have from his sulphate series, as equivalent to 100 parts of $BaSO_4$, the amounts of Tl_2SO_4 given in the third column:

* Zeit. Anal. Chem., 2, 211. 1863.
† Ann. Chem. Pharm., 134, 11. 1865.

1.4195 grm. Tl_2SO_4 gave	.6534 grm. $BaSO_4$.			217.248
1.1924 "	.5507 "			216.524
.8560 "	.3957 "			216.325
			Mean,	216.699

Including Lamy's single result, as of equal weight, we get a mean of 216.754. ± .1387.

From the chloride series we have these results, with the ratio stated as usual:

.2984 grm. TlCl gave	.1791 grm. AgCl.		166.611
.5452 "	.3278 . "		166.321
		Mean,	166.465, ± .097

Lamy's mean was 166.915, ± .1905. Both means combined give a general mean of 166.555, ± .0865.

Werther's* determinations of iodine in thallium iodide were made by two methods. In the first series TlI was decomposed by zinc and potassium hydroxide, and in the filtrate the iodine was estimated as AgI. One hundred parts of AgI correspond to the amounts of TlI given in the last column:

.720 grm. TlI gave	.51 grm. AgI.		141.176
2.072 "	1.472 "		140.761
.960 "	.679 "		141.384
.385 "	.273 "		141.026
1.068 "	.759 "		140.711
		Mean,	141.012, ± .085

In the second series the thallium iodide was decomposed by ammonia in presence of silver nitrate, and the resulting AgI was weighed. Expressed according to the foregoing standard the results are as follows:

1.375 grm. TlI gave	.978 grm. AgI.	Ratio,	140.593
1.540 "	1.095 "		140.639
1.380 "	.981 "		140.673
		Mean,	140.635, ± .016

General mean of both series, 140.648, ± .016.

* Journ. für Prakt. Chem., 92, 128. 1864.

From the foregoing results three values for the atomic weight of thallium are calculable:

From the sulphate	Tl =	204.169, ± .166
From the chloride	" =	203.879, ± .126
From the iodide	" =	203.886, ± .054

In 1873 Crookes,* the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities from absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed especially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly in vacuo, but all were reduced to *absolute* standards; and unusually large quantities of thallium were employed in each experiment. In short, no effort was spared to attain as nearly as possible absolute precision of results. The details of the investigation are too voluminous, however, to be cited here; the reader who wishes to become familiar with them must consult the original memoir. Suffice it to say that the research is a model which other chemists will do well to copy.

The results of ten experiments by Professor Crookes may be stated as follows. In a final column we may state the quantity of nitrate producible from 100 parts of thallium. The weights given are in grains:

Thallium.	*$TlNO_3$ + Glass.*	*Glass Vessel.*	*Ratio.*
497.972995	1121.851852	472.557319	130.3875
293.193507	1111.387014	729.082713	130.3930
288.562777	971.214142	594.949719	130.3926
324.963740	1142.569408	718.849078	130.3900
183.790232	1005.779897	766.133831	130.3912
190.842532	997.334615	748.491271	130.3920
195.544324	1022.176679	767.203451	130.3915
201.816345	1013.480135	750.332401	130.3897
295.683523	1153.947672	768.403621	130.3908
299.203036	1159.870052	769.734201	130.3917
		Mean,	130.3910, ± .00034

* Philosophical Transactions, 1873, p. 277.

Hence, using the atomic weights and probable errors previously found for N and O, Tl = 203.715, ± .0365. If O = 16, Tl = 204.183.

Crookes himself, using 61.889 as the molecular weight of the group NO_3, gets the value Tl = 203.642; the lowest value in the series being 203.628, and the highest 203.666: an extreme variation of 0.038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes' work is concerned. But its value depends in reality upon the accuracy of other chemists in fixing the atomic weights of N and O; a slight variation in either of the latter constants producing a large variation here. What Crookes really has done has been to fix with almost absolute certainty the ratio between Tl and NO_3. If the latter group should have the molecular weight 62, in accordance with Prout's hypothesis, then Tl = 204.008. In other words, the ratio thus fixed by Crookes is almost exactly represented by two whole numbers, and supports Prout's hypothesis in a very decided way. Crookes himself seems to have overlooked this fact, for he regards his results as militating against the hypothesis in question.

GLUCINUM.

The atomic weight of glucinum is at present much in doubt; our knowledge of it depending upon the unsettled question whether the oxide is GlO or Gl_2O_3. The formula GlO agrees with Mendelejeff's law, and is advocated by Reynolds,* Lothar Meyer,† and Brauner.‡ The symbol Gl_2O_3, on the other hand, is favored by Nilson and Pettersson,‖ and by Humpidge.§ Humpidge, Meyer, and Brauner

* Phil. Mag., (5,) 3, 38. 1877. Chem. News, 42, 273. 1880.

† Ber. der Deutsch. Chem. Gesell., 13, 1780. 1880. Also, 11, 576. 1879.

‡ Phil. Mag., (5,) 11. Jan., 1881.

‖ Berichte, 11, 381 and 906. 1879. Also, 13, 2035. 1880.

§ Chem. News, 42, 261. 1880.

offer only theoretical discussions of the subject; Reynolds and Nilson and Pettersson have determined the specific heat of the metal, but give opposed results. In the following calculations the simpler formula will be assumed, not as a finality, but because of its accordance with the system of Mendelejeff.

The data from which we are to calculate the atomic weight of glucinum have been determined by Awdejew, Weeren, Klatzo, Debray, and Nilson and Pettersson. Berzelius'* single experiment on the sulphate may be left out of account.

Awdejew,† whose determination was the earliest of any value, analyzed the sulphate. The sulphuric acid was thrown down as barium sulphate; and in the filtrate, from which the excess of barium had been first removed, the glucina was precipitated by ammonia. The figures which Awdejew publishes represent the ratio between SO_3 and GlO, but not absolute weights. As, however, his calculations were made with $SO_3 = 501.165$, and Ba probably $=$ 855.29, we may add a third column showing how much $BaSO_4$ is proportional to 100 parts of GlO:

SO_3.	*GlO.*	*Ratio.*
4457	1406	921.242
4531	1420	927.304
7816	2480	915.903
12880	4065	920.814
		Mean, 921.316, $\pm$ 1.577

The same method was followed by Weeren and by Klatzo, except that Weeren used ammonium sulphide instead of ammonia for the precipitation of the glucina. Weeren‡ gives the following weights of GlO and $BaSO_4$. The ratio is given in a third column, just as with the figures by Awdejew:

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* Poggend. Annal., 8, 1.
† " 56, 106. 1842.
‡ " 92, 124. 1854.

GlO.	*BaSO$_4$.*	*Ratio.*
.3163 grm.	2.9332 grm.	927.031
.2872 "	2.6377 "	918.419
.2954 "	2.7342 "	925.592
.5284 "	4.8823 "	902.946

Mean, 918.497, ± 3.624

Klatzo's* figures are as follows, with the third column added by the writer:

GlO.	*BaSO$_4$.*	*Ratio.*
.2339 grm.	2.1520 grm.	920.052
.1910 "	1.7556 "	919.162
.2673 "	2.4872 "	930.490
.3585 "	3.3115 "	923.710
.2800 "	2.5842 "	922.989

Mean, 923.281, ± 1.346

Combining these series into a general mean, we get the subjoined result:

Awdejew	921.316, ± 1.577
Weeren	918.497, ± 3.624
Klatzo	923.281, ± 1.346
General mean	922.164, ± 0.985

Hence GlO = 25.224, ± .269.

Debray† analyzed a double oxalate of glucinum and ammonium, $Gl(NH_4)_2C_4O_8$. In this the glucina was estimated by calcination, after first converting the salt into nitrate. The following percentages were found:

11.5
11.2
11.6

Mean, 11.433, ± .081

The carbon was estimated by an organic combustion. I give the weights, and put in a third column the percentages of CO_2 thus obtained:

* Zeitschrift für Anal. Chem., 8, 523. 1869.

† Ann. de Chim. et de Phys., (3,) 44, 37. 1855.

Salt.	CO_2.	*Per cent.* CO_2.
.600 grm.	.477 grm.	79.500
.603 "	.478 "	79.270
.600 "	.477 "	79.500
		Mean, 79.423, ± .052

Calculating the ratio between CO_2 and GlO, we have for the molecular weight of the latter, GlO = 25.220, ± .180. The agreement between this result and the one previously deduced from the sulphate is certainly very striking.

Last of all and best of all we come to the determinations recently published by Nilson and Pettersson.* These chemists sought to use the sublimed chloride of glucinum, but found it to contain traces of lime derived from a glass tube. They finally resorted to the sulphate as the most available salt for their purposes. This, which they write $Gl_2(SO_4)_3$ $12H_2O$, and which we formulate as $GlSO_4.4H_2O$, yields pure glucina upon strong ignition. The subjoined percentages of glucina were thus obtained:

14.171
14.169
14.160
14.176

Mean, 14.169, ± .0023

Hence GlO = 25.048, and Gl = 9.085, ± .0055. If O = 16, Gl = 9.106. If SO_3 = 80, then Gl = 9.096.

If the oxide is Gl_2O_3, then the value Gl = 9.085, ± .0055 becomes Gl = 13.628, ± .0082.

It would be easy enough to combine this value for Gl with those derived from the experiments of the investigators previously cited, but it is hardly worth while. All the other estimations have such high probable errors that they would practically vanish from the general mean. Their influence would hardly extend to the third decimal place, and they may therefore be neglected.

* Compt. Rend., 91, 168. 1880.

MAGNESIUM.

There is perhaps no common metal of which the atomic weight has been subjected to closer scrutiny than that of magnesium. The value is low, and its determination should, therefore, be relatively free from many of the ordinary sources of error; it is extensively applied in chemical analysis, and ought consequently to be accurately ascertained. Strange discrepancies, however, exist between the results obtained by different investigators; so that the generally accepted figure cannot be regarded as absolutely free from doubt.

The determinations of Berzelius* and other early chemists need not be here considered. Nor does the estimation made by Macdonnell† deserve more than a passing mention. He puts the atomic weight of magnesium at 23.9, but gives no details concerning his method of determination. The researches which we have to consider are those of Scheerer, Svanberg and Nordenfeldt, Jacquelain, Bahr, Marchand and Scheerer, and Dumas.

Scheerer's method of investigation was exceedingly simple.‡ He merely estimated the sulphuric acid in anhydrous magnesium sulphate, employing the usual process of precipitation as barium sulphate. He gives no weighings, but reports the percentages of SO_3 thus found. In his calculations, O = 100, SO_3 = 500.75, and BaO = 955.29. It is easy, therefore, to recalculate the figures which he gives, so as to establish what his method really represents, viz., the ratio between the sulphates of barium and magnesium.

Thus revised, his four analyses show that 100 parts of $MgSO_4$ yield the following quantities of $BaSO_4$:

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* Lehrbuch, 5 Aufl., Bd. 3, s. 1227.

† British Association Report, 1852, part 2, p. 36.

‡ Poggend. Annal., 69, 535. 1846.

	Per cent. SO_3.
193.575	66.573
193.677	66.608
193.767	66.639
193.631	66.592

Mean, 193.6625, ± .0274

Hence, using the atomic weights deduced in previous chapters for Ba, S, and O, Mg = 24.544, ± .0311. In a subsequent note* Scheerer shows that the barium sulphate of the foregoing experiments carried down with it magnesium salts in such quantity as to make the atomic weight of magnesium 0.39 too low. Corrected, Mg becomes = 24.545.

The work of Bahr, of Jacquelain, and in part that of Svanberg and Nordenfeldt, also relates to the composition of magnesium sulphate. Jacquelain's experiments were as follows.† Dry magnesium sulphate was prepared by mixing the ordinary hydrous salt to a paste with sulphuric acid, and calcining the mass in a platinum crucible over a spirit lamp to constant weight and complete neutrality of reaction. This dry sulphate was weighed and intensely ignited three successive times. The weight of the residual MgO having been determined, it was moistened with sulphuric acid and recalcined over a spirit lamp, thus reproducing the original weight of $MgSO_4$. Jacquelain's weighings for these two experiments show that 100 parts of MgO correspond to the quantities of $MgSO_4$ given in the last column:

1.466 grm. $MgSO_4$ gave .492 grm. MgO.	297.968
.492 " MgO " 1.466 " $MgSO_4$.	297.968

Jacquelain also made one estimation of sulphuric acid in the foregoing sulphate as $BaSO_4$. His result, (1.464 grm. $MgSO_4$ = 2.838 grm. $BaSO_4$,) reduced to the standard adopted in dealing with Scheerer's experiments, give for 100 parts of $MgSO_4$, 193.852 $BaSO_4$. If this figure be given equal weight with a single experiment in Scheerer's series,

* Poggend. Annal., 70, 407.

† Ann. d. Chim. et Phys., 3 serie, 32, 202.

and combined with the latter, the mean will be 193.700, $\pm$ .0331. From this the atomic weight of magnesium becomes 24.244, $\pm$ .033. This again, corrected according to Scheerer for the magnesium salts carried down by the barium sulphate, becomes 0.39 higher, or Mg = 24.283. Of course this correction, determined by Scheerer for a single experiment, can only be a rough approximation in a mean like the foregoing. It is better than no correction at all, the character of the error involved being known.

Bahr's* work resembles in part that of Jacquelain. This chemist converted pure magnesium oxide into sulphate, and from the increase in weight determined the composition of the latter salt. From his weighings 100 parts of MgO equal the amounts of $MgSO_4$ given in the third column:

1.6938 grm. MgO gave	5.0157 grm. $MgSO_4$.	296.122
2.0459 "	6.0648 "	296.437
1.0784 "	3.1925 "	296.040
		Mean, 296.200, $\pm$ .0815

About four years previous to the investigations of Bahr the paper of Svanberg and Nordenfeldt† appeared. These chemists started with the oxalate of magnesium, which was dried at a temperature of from 100° to 105° until it no longer lost weight. The salt then contained two molecules of water, and upon strong ignition it left a residue of MgO. The percentage of MgO in the oxalate comes out as follows:

7.2634 grm. oxalate gave	1.9872 grm. oxide.	27.359 per cent.
6.3795 "	1.7464 "	27.375 "
6.3653 "	1.7418 "	27.364 "
6.2216 "	1.7027 "	27.368 "
		Mean, 27.3665, $\pm$ .0023

In three of these experiments the MgO was treated with H_2SO_4, and converted, as by Jacquelain and by Bahr in their later researches, into $MgSO_4$. One hundred parts of MgO gave of $MgSO_4$ as follows:

* Journ. für Prakt. Chem., 56, 310. 1852.
† Journ. für Prakt. Chem., 45, 473. 1848.

1.9872 grm. MgO gave	5.8995 grm. $MgSO_4$.	296.875
1.7464 "	5.1783 "	296.513
1.7418 "	5.1666 "	296.624
	Mean,	296.671, $\pm$ .072

We have now for this ratio between MgO and $MgSO_4$ three series; not at all concordant. We may combine them, assigning to each of Jacquelain's two results a weight corresponding to one of Bahr's:

Jacquelain	297.968, $\pm$ .0999
Bahr	296.200, $\pm$ .0815
Svanberg and Nordenfeldt	296.671, $\pm$ .072
General mean	296.806, $\pm$ .0475

In 1850 the elaborate investigations of Marchand and Scheerer* appeared. These chemists undertook to determine the composition of some natural magnesites, and, by applying corrections for impurities, to deduce from their results the sought for atomic weight. The magnesite chosen for the investigation was, first, a yellow, transparent variety from Snarum; second, a white opaque mineral from the same locality; and, third, a very pure quality from Frankenstein. In each case the impurities were carefully determined; but only a part of the details need be cited here. Silica was of course easily corrected for by simple subtraction from the sum of all of the constituents; but iron and calcium, when found, having been present in the mineral as carbonates, required the assignment to them of a portion of the carbonic acid. In the atomic weight determinations the mineral was first dried at 300°. The loss in weight upon ignition was then carbon dioxide. It was found, however, that even here a correction was necessary. Magnesite, upon drying at 300°, loses a trace of CO_2, and still retains a little water; on the other hand, a minute quantity of CO_2 remains even after ignition. The CO_2 expelled at 300° amounted in one experiment to .054 per cent.; that retained after calcination to .055 per cent. Both errors tend in the

* Journ. für Prakt. Chem., 50, 385.

same direction, and increase the apparent percentage of MgO in the magnesite. On the yellow mineral from Snarum the crude results are as follows, giving percentages of MgO, FeO, and CO_2 after eliminating silica:

CO_2.	*MgO.*	*FeO.*
51.8958	47.3278	.7764
51.8798	47.3393	.7809
51.8734	47.3154	.8112
51.8875	47.3372	.7753
	Mean, 47.3299 ± .0037	

After applying corrections for loss and retention of CO_2, as previously indicated, the mean results of the foregoing series become—

CO_2.	*MgO.*	*FeO.*
51.9931	47.2743	.7860

The ratio between the MgO and the CO_2, after correcting for the iron, will be considered further on.

Of the white magnesite from Snarum but a single analysis was made, which, for present purposes may be ignored. Concerning the Frankenstein mineral three series of analyses were executed. In the first series the following results were obtained:

8.996 grm. CO_2 =	8.2245 grm. MgO.	47.760 per cent. MgO.
7.960 "	7.2775 "	47.761 "
9.3265 "	8.529 "	47.767 "
7.553 "	6.9095 "	47.775 "
		Mean, 47.766, ± .0022

This mean, corrected for loss of CO_2 in drying, becomes 47.681. I give series second with corrections applied:

6.8195 grm. $MgCO_3$ gave	3.2500 grm. MgO.	47.658 per cent.
11.3061 "	5.3849 "	47.628 "
9.7375 "	4.635 "	47.599 "
12.3887 "	5.9033 "	47.650 "
32.4148 "	15.453 "	47.674 "
38.8912 "	18.5366 "	47.663 "
26.5223 "	12.6445 "	47.675 "
		Mean, 47.650, ± .0069

The third series was made upon very pure material, so that the corrections, although applied, were less influential. The results were as follows:

4.2913 grm.	$MgCO_3$ gave	2.0436 grm.	MgO.	47.622 per cent.
27.8286	"	13.2539	"	47.627 "
14.6192	"	6.9692	"	47.672 "
18.3085	"	8.7237	"	47.648 "
				Mean, 47.642, $\pm$ .0077

In a supplementary paper* by Scheerer, it was shown that an important correction to the foregoing data had been overlooked. Scheerer, re-examining the magnesites in question, discovered in them traces of lime, which had escaped notice in the original analyses. With this correction the two magnesites in question exhibit the following mean composition:

	Snarum.	*Frankenstein.*
CO_2	52.131	52.338
MgO	46.663	47.437
CaO	.430	.225
FeO	.776	----
	100.000	100.000

Correcting for lime and iron, by assigning each its share of CO_2, the Snarum magnesite gives as the true percentage of magnesia in pure magnesium carbonate, the figure 47.624. To this, without serious mistake, we may assign the weight indicated by the probable error, $\pm$ .0037; the quantity previously deduced from the percentages of MgO given in the uncorrected analyses.

From the Frankenstein mineral, similarly corrected, the final mean percentage of MgO in $MgCO_3$ becomes 47.628. This, however, represents three series of analyses, whose combined probable errors may be properly assigned to it. The combination is as follows:

* Ann. d. Chem. und Pharm., 110, 240.

$\pm .0022$
$\pm .0069$
$\pm .0077$

Result, $\pm .0020$, probable error of the general mean.

We may now combine the results obtained from both magnesites:

Snarum mineral.......	Per cent. MgO,	47.624, $\pm$ .0037
Frankenstein mineral ..	"	47.628, $\pm$ .0020
General mean....	"	47.627, $\pm$ .0018

The last investigation upon the atomic weight of magnesium which we have to consider is that of Dumas.* Pure magnesium chloride was placed in a boat of platinum, and ignited in a stream of dry hydrochloric acid gas. The excess of the latter having been expelled by a current of dry carbon dioxide, the platinum boat, still warm, was placed in a closed vessel and weighed therein. After weighing, the chloride was dissolved and titrated in the usual manner with a solution containing a known quantity of pure silver. The weighings which Dumas reports give, as proportional to 100 parts of silver, the quantities of $MgCl_2$ stated in the third column:

2.203 grm. $MgCl_2$ =	4.964	grm. Ag.		44.380
2.5215 "	5.678	"		44.408
2.363 "	5.325	"		44.376
3.994 "	9.012	"		44.319
2.578 "	5.834	"		44.189
2.872 "	6.502	"		44.171
2.080 "	4.710	"		44.161
2.214 "	5.002	"		44.262
2.086 "	4.722	"		44.176
1.688 "	3.823	"		44.154
1.342 "	3.031	"		44.276
			Mean,	44.261, $\pm$ .020

There are now before us the following ratios, from which to deduce the sought-for atomic weight:

* Ann. Chem. Pharm., 113, 33. 1860.

(1.) $MgSO_4 : BaSO_4 :: 100 : 193.700, \pm .0331$
(2.) $MgO : MgSO_4 :: 100 : 296.806, \pm .0475$
(3.) Per cent. of MgO in oxalate, 27.3665, $\pm$ .0023
(4.) Per cent. of MgO in carbonate, 47.627, $\pm$ .0018
(5.) $Ag : MgCl_2 :: 100 : 44.261, \pm .020$

From these we find three values for the molecular weight of MgO:

From (2)	MgO	= 40.587, $\pm$ .0126
From (3)	"	= 40.603, $\pm$ .0069
From (4)	"	= 39.922, $\pm$ .0030
General mean	"	= 40.054, $\pm$ .0027

We have also three values for the atomic weight of magnesium:

From molecular weight of MgO	Mg	= 24.091, $\pm$ .0044
From ratio (1,) corrected	"	= 24.283, $\pm$ .033
From ratio (5,) Dumas	"	= 24.576, $\pm$ .032
General mean	"	= 24.103, $\pm$ .0043

Or, if O = 16, Mg becomes = 24.159.

In this general mean all the determinations are included, good or bad. Dumas' result is unquestionably wrong; the error, probably, being due to the presence of oxychloride in the $MgCl_2$ which was used. It is doubtful whether any precautions could have eliminated that error. If we take only Marchand and Scheerer's work on magnesium carbonate as having positive value, we shall get from their analyses the following result, viz: Mg = 23.959, $\pm$ .0046. Or, if O = 16, this becomes 24.014. The atomic weight of magnesium, therefore, varies from the whole number 24, only within the ordinary limits of experimental error.

ZINC.

The several determinations of the atomic weight of zinc are by no means closely concordant. The results obtained by Gay-Lussac* and Berzelius† were undoubtedly too low, and may be disregarded here. We need consider only the work done by Jacquelain, Favre, and Axel Erdmann.

In 1842 Jacquelain published the results of his investigations upon this important constant.‡ In two experiments a weighed quantity of zinc was converted into nitrate, and that by ignition in a *platinum* crucible was reduced to oxide. In two other experiments sulphuric acid took the place of nitric. As the zinc contained small quantities of lead and iron, these were estimated, and the necessary corrections applied. From the weights of metal and oxide given by Jacquelain the percentages have been calculated:

		Nitric Series.	
9.917 grm. Zn	gave	12.3138 grm. ZnO.	80.536 per cent. Zn.
9.809	"	12.1800 "	80.534 "
		Sulphuric Series.	
2.398	"	2.978 grm. ZnO.	80.524 "
3.197	"	3.968 "	80.570 "
		Mean of all four,	80.541, ± .007

Hence Zn = 66.072, ± .028.

The method adopted by Axel Erdmann‖ is essentially the same as that of Jacquelain, but varies from the latter in certain important details. First, pure zinc oxide was prepared, ignited in a covered crucible with sugar, and then, to complete the reduction, ignited in a porcelain tube in a current of hydrogen. The pure zinc thus obtained was converted into oxide by means of treatment with nitric acid and sub-

* Mémoire d'Arceuil, 2, 174.

† Gilb. Annal., 37, 460.

‡ Compt. Rend., 14, 636.

‖ Poggend. Annal., 62, 611. Berz. Lehrb., 3. 1219.

sequent ignition in a *porcelain* crucible. Erdmann's figures give us the following percentages of metal in the oxide:

80.247
80.257
80.263
80.274

Mean, 80.260, ± .0037

Hence Zn = 64.9045, ± .019.

If we combine the results of Jacquelain with those of Erdmann, we get a mean percentage of zinc, 80.324, ± .0032; and an atomic weight of Zn = 65.168, ± .018. The reason for the discordance between the two experimenters will be considered further along.

Favre* employed two methods of investigation. First, zinc was dissolved in sulphuric acid, the hydrogen evolved was burned, and the weight of water thus formed was determined. To his weighings I append the ratio between metallic zinc and 100 parts of water:

25.389 grm. Zn gave	6.928 grm. H_2O.	366.469
30.369 "	8.297 "	366.024
31.776 "	8.671 "	366.463

Mean, 366.319, ± .088

Hence Zn = 65.803, ± .020.

The second method adopted by Favre was to burn pure zinc oxalate, and to weigh the oxide and carbonic acid thus produced. From the ratio between these two sets of weights the atomic weight of zinc is easily deducible. From Favre's weighings, if CO_2 = 100, ZnO will be as given in the third column below:

7.796 grm. ZnO =	8.365 grm. CO_2.	93.198
7.342 "	7.883 "	93.137
5.2065 "	5.588 "	93.173

Mean, 93.169, ± .012

Hence Zn = 65.8395, ± .022.

* Ann. Chim. Phys., (3,) 10, 163. 1844.

A fourth combustion of the oxalate is omitted from the above series, having been rejected by Favre himself. In this the oxide formed was contaminated by traces of sulphide.

The four values for zinc now before us are so discordant that a combination of them after the usual method can have only a trifling significance. The following is the result thus obtained:

From Jacquelain's figures	Zn =	66.072,	± .028
From Favre's water series	" =	65.803,	± .020
From Favre's oxalate series	" =	65.8395,	± .022
From Erdmann's figures	" =	64.9045,	± .019
General mean	" =	65.557,	± .011

It will be seen that three of these values agree tolerably well, placing the atomic weight of zinc in the neighborhood of 66, while the other is, in round numbers, about a unit lower. This lower figure, however, has the smallest probable error, and it will be found also, upon careful consideration, that it is less likely than the others to be vitiated by experimental inaccuracies. Both chemically and mathematically it is the best.

Upon comparing Erdmann's results with those of Jacquelain two points are worth noticing: first, Erdmann worked with purer material than Jacquelain, although the latter applied corrections for the impurities which he knew were present; secondly, Erdmann calcined his zinc nitrate in a porcelain crucible, while Jacquelain used platinum. In the latter case it has been shown that portions of zinc may become reduced and alloy themselves with the platinum of the crucible. Hence a lower weight of oxide from a given quantity of zinc, a higher percentage of metal, and an increased atomic weight. This source of constant error has undoubtedly affected Jacquelain's experiments, and vitiated his results. In Erdmann's work no such errors seem to be present.

Over Favre's experiments Erdmann's have the important merit of simplicity. In the latter it is difficult to detect sources of error; in the former it is easy. In Favre's water

series it was essential that the hydrogen should first be thoroughly dried before combustion, and then that every trace of water formed should be collected. A trivial loss of hydrogen or of water would tend to increase the apparent atomic weight of zinc.

In the combustion of the zinc oxalate equally great difficulties are encountered. Here a variety of errors are possible, such as are due, for example, to impurity of material, to imperfect drying of the carbon dioxide, and to incomplete collection of the latter. It may not be easy to prove that such errors actually did creep into Favre's work, and yet their possibility hinders us from absolutely accepting his results.

All things considered, then, Erdmann's determination of the atomic weight of zinc is the one most entitled to credit, and must be taken for the present in lieu of the general mean deduced from all four of the values. This determination, Zn = 64.9045, ± .019, becomes, if O = 16, 65.054.

CADMIUM.

The earliest determination of the atomic weight of this metal was by Stromeyer, who found that 100 parts of cadmium united with 14.352 of oxygen.* With our value for the atomic weight of oxygen these figures make Cd = 111.227. This result has now only a historical interest.

The more modern estimates of the atomic weight of cadmium are four in number, by v. Hauer, Lenssen, Dumas, and Huntington. Of these that by v. Hauer† comes first in chronological order. He heated pure anhydrous cadmium sulphate in a stream of dry hydrogen sulphide, and weighed the cadmium sulphide thus obtained. His results

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* See Berz. Lehrbuch, 5th Ed., 3, 1219.

† Journ. für Prakt. Chem., 72, 350. 1857.

were as follows, with the percentage of CdS in $CdSO_4$ therefrom deduced:

7.7650 grm. $CdSO_4$ gave	5.3741 grm. CdS.	69.209 per cent.
6.6086 "	4.5746 "	69.222 "
7.3821 "	5.1117 "	69.245 "
6.8377 "	4.7336 "	69.228 "
8.1956 "	5.6736 "	69.227 "
7.6039 "	5.2634 "	69.220 "
7.1415 "	4.9431 "	69.217 "
5.8245 "	4.0335 "	69.251 "
6.8462 "	4.7415 "	69.257 "

Mean, 69.231, ± .0042

Lenssen* worked upon pure cadmium oxalate, handling, however, only small quantities of material. This salt, upon ignition, leaves the following percentages of oxide:

.5128 grm. oxalate gave	.3281 grm. CdO.	63.982 per cent.
.6552 "	.4193 "	63.996 "
.4017 "	.2573 "	64.053 "

Mean, 64.010, ± .014

Dumas† dissolved pure cadmium in hydrochloric acid, evaporated the solution to dryness, and fused the residue in hydrochloric acid gas. The cadmium chloride thus obtained was dissolved in water and titrated with a solution of silver after the usual manner. From Dumas' weighings I calculate the ratio between $CdCl_2$ and 100 parts of silver:

2.369 grm. $CdCl_2$ =	2.791 grm. Ag.	84.880
4.540 "	5.348 "	84.892
6.177 "	7.260 "	85.803
2.404 "	2.841 "	84.618
3.5325 "	4.166 "	84.794
4.042 "	4.767 "	84.791

Mean, 84.843, ± .026

Latest of all comes Huntington's‡ work, done under the direction of Professor J. P. Cooke. Bromide of cadmium

* Journ. für Prakt. Chem., 79, 281. 1860.
† Ann. Chem. Pharm., 113, 27. 1860.
‡ Proc. Amer. Acad., 1881.

was prepared by dissolving the carbonate in hydrobromic acid, and the product, dried at 200°, was purified by sublimation in a porcelain tube. Upon the compound thus obtained two series of experiments were made.

In one series the bromide was dissolved in water, and a quantity of silver not quite sufficient for complete precipitation of the bromine was then added in nitric acid solution. After the precipitate had settled, the supernatant liquid was titrated with a standard solution of silver containing one gramme to the litre. The precipitate was washed by decantation, collected by reverse filtration, and weighed. To the weighings I append the ratio between $CdBr_2$ and 100 parts of silver bromide:

1.5592 grm.	$CdBr_2$ gave	2.1529 grm.	AgBr.	Ratio, 72.423
* 3.7456	"	5.1724	"	72.415
2.4267	"	3.3511	"	72.415
* 3.6645	"	5.0590	"	72.435
* 3.7679	"	5.2016	"	72.437
2.7938	"	3.8583	"	72.410
* 1.9225	"	2.6552	"	72.405
3.4473	"	4.7593	"	72.433

Mean, 72.4216, ± .0028

The second series was like the first, except that the weight of silver needed to effect precipitation was noted, instead of the weight of silver bromide formed. In the experiments marked with an asterisk, both the amount of silver required and the amount of silver bromide thrown down were determined in one set of weighings. The third column gives the $CdBr_2$ proportional to 100 parts of silver:

* 3.7456 grm.	$CdBr_2$ =	2.9715 grm.	Ag.	126.051
5.0270	"	3.9874	"	126.072
* 3.6645	"	2.9073	"	126.045
* 3.7679	"	2.9888	"	126.067
* 1.9225	"	1.5248	"	126.082
2.9101	"	2.3079	"	126.093
3.6510	"	2.8951	"	126.110
3.9782	"	3.1551	"	126.088

Mean, 126.076, ± .0052

From the first series	$CdBr_2$	= 271.498,	± .032
From the second series	"	= 271.505,	± .027
General mean	"	= 271.502,	± .0215

Hence Cd = 111.966, ± .043.

According to Huntington's own calculations these experiments fix the ratio between silver, bromine, and cadmium as Ag : Br : Cd : : 108 : 80 : 112.31. This result militates strongly against Prout's hypothesis.

Upon combining all the determinations we get the following result:

v. Hauer	Cd	= 111.684,	± .040
Lenssen	"	= 111.803,	± .062
Dumas	"	= 111.969.	± .065
Huntington	"	= 111.966,	± .040
General mean	"	= 111.835,	± .024

Or, if O = 16, then Cd = 112.092.

It will be seen that Dumas and Huntington's determinations, both made with haloid salts of cadmium, agree with wonderful closeness, and so confirm each other. On the other hand, v. Hauer's data give a value for the atomic weight of cadmium which is much lower. Apparently, v. Hauer's method was good, and the reason for the discrepancy remains to be discovered. Until it is ascertained I prefer to use the above mean value for Cd, rather than to adopt one investigation and reject the others.

MERCURY.

In dealing with the atomic weight of mercury we may reject the early determinations by Sefström* and a large part of the work done by Turner.† The latter chemist, in addition to the data which will be cited below, gives figures

* Sefström. Berz. Lehrb., 5th Ed., 3, 1215. Work done in 1812.

† Phil. Trans., 1833, 531–535.

to represent the percentage composition of both the chlorides of mercury; but these results are neither reliable nor in proper shape to be used.

First in order we may consider the percentage composition of mercuric oxide, as established by Turner and by Erdmann and Marchand. In both investigations the oxide was decomposed by heat, and the mercury was accurately weighed. Gold leaf served to collect the last traces of mercurial vapor.

Turner gives four estimations.* Two represent oxide obtained by the ignition of the nitrate, and two are from commercial oxide. In the first two the oxide still contained traces of nitrate, but hardly in weighable proportions. A comparison of the figures from this source with the others is sufficiently conclusive on this point. The third column represents the percentage of mercury in HgO:

144.805 grains Hg =	11.54 grains O.	92.619 per cent.
125.980 "	10.08 "	92.592 "
173.561 "	13.82 "	92.625 "
114.294 "	9.101 "	92.620 "
		Mean, 92.614, ± .0050

In the experiments of Erdmann and Marchand † every precaution was taken to ensure accuracy. Their weighings, reduced to a vacuum standard, give the subjoined percentages:

82.0079 grm. HgO gave	75.9347 grm. Hg.	92.594 per cent.
51.0320 "	47.2538 "	92.597 "
84.4996 "	78.2501 "	92.604 "
44.6283 "	41.3285 "	92.606 "
118.4066 "	109.6408 "	92.597 "
		Mean, 92.5996, ± .0015

Combining, we have:

Turner	92.614, ± .0050
Erdmann and Marchand	92.5996, ± .0015
General mean	92.601, ± .0014

* Phil. Trans., 1833, 531–535.

† Journ. für Prakt. Chem., 31, 395. 1844.

With a view to establishing the atomic weight of sulphur Erdmann and Marchand also made a series of analyses of pure mercuric sulphide. These data are now best available for discussion under mercury. The sulphide was mixed with pure copper and ignited; mercury distilling over and copper sulphide remaining behind. Gold leaf was used to retain traces of mercurial vapor, and the weighings were reduced to vacuum:

34.3568 grm. HgS gave	29.6207 grm. Hg.	86.215 per cent. Hg.
24.8278 "	21.40295 "	86.206 "
37.2177 "	32.08416 "	86.207 "
80.7641 "	69.6372 "	86.223 "
	Mean,	86.2127, ± .0027

For the percentage of mercury in mercuric chloride we have data by Turner, Millon, and Svanberg. Turner,* in addition to some precipitations of mercuric chloride by silver nitrate, gives two experiments in which the compound was decomposed by pure stannous chloride, and the mercury thus set free was collected and weighed. The results were as follows:

44.782 grains Hg =	15.90 grains Cl.	73.798 per cent.
73.09 "	25.97 "	73.784 "
	Mean,	73.791, ± .005

Millon† purified mercuric chloride by solution in ether and sublimation, and then subjected it to distillation with lime. The mercury was collected as in Erdmann and Marchand's experiments. Percentages of metal as follows:

73.87
73.81
73.83
73.87

Mean, 73.845, ± .010

Svanberg,‡ following the general method of Erdmann

* Phil. Trans., 1833, 531-535.
† Ann. Chim. Phys., (3,) 18, 345 1846.
‡ Journ. für Prakt. Chem., 45, 472. 1848.

and Marchand, made three distillations of mercuric chloride with lime, and got the following results:

12.048 grm. $HgCl_2$ gave	8.889 grm. Hg.	73.780 per cent.
12.529 "	9.2456 "	73.794 "
12.6491 "	9.3363 "	73.810 "
		Mean, 73.795, ± .006

Combining these series we have:

Turner	73.791, ± .005
Millon	73.845, ± .010
Svanberg	73.795, ± .006
General mean	73.798, ± .0034

In this mean Turner's figures undoubtedly receive undue weight, for, on experimental grounds, they are probably inferior to both of the other series. It is better, however, that the general mean should remain as it is, than that I should deal arbitrarily with any of the data.

We now have three figures to calculate from:

Per cent. of Hg in HgO	92.601, ± .0014
" HgS	86.2127, ± .0027
" $HgCl_2$	73.798, ± .0034

These give us three values for the atomic weight of mercury and a general mean as follows:

From HgO	Hg = 199.786, ± .059
From HgS	" = 200.016, ± .088
From $HgCl_2$	" = 199.239, ± .086
General mean	" = 199.712, ± .042

If O = 16, then this becomes 200.171.

CHROMIUM.

Concerning the atomic weight of chromium there has been much discussion, and many experimenters have sought to establish the true value. The earliest work upon it hav-

ing any importance was that of Berzelius,* in 1818 and 1826, which led to results much in excess of the correct figure. His method consisted in precipitating a known weight of lead nitrate with an alkaline chromate and weighing the lead chromate thus produced. The error in his determination arose from the fact that lead chromate, except when thrown down from very dilute solutions, carries with it minute quantities of alkaline salts, and so has its apparent weight notably increased. When dilute solutions are used, a trace of the precipitate remains dissolved, and the weight obtained is too low. In neither case is the method trustworthy.

In 1844 Berzelius' results were first seriously called in question. The figure for chromium deduced from his experiments was somewhat over 56; but Peligot† now showed, by his analyses of chromous acetate and of the chlorides of chromium, that the true number was near 52.5. Unfortunately, Peligot's work, although good, was published with insufficient details to be useful here. For chromous acetate he gives the percentages of carbon and hydrogen, but not the actual weights of salt, carbon dioxide, and water from which they were calculated. His figures vary considerably moreover; enough to show that their mean would carry but little weight when combined with the more explicit data furnished by other chemists.

Jacquelain's‡ work we may omit entirely. He gives an atomic weight for chromium which is notoriously too low, and prints none of the numerical details upon which his result rests. The researches which particularly command our attention are those of Berlin, Moberg, Lefort, Wildenstein, Kessler, and Siewert.

Among the papers upon the atomic weight under consideration that by Berlin is one of the most important.‖ His starting point was normal silver chromate; but in one ex-

* Schweigg. Journ., 22, 53, and Poggend. Annal., 8, 22.

† Compt. Rend., 19, 609 and 734; 20, 1187; 21, 74.

‡ Compt. Rend., 24, 679. 1847.

‖ Journ. für Prakt. Chem., 37, 509, and 38, 149. 1846.

periment the anhydrochromate $Ag_2Cr_2O_7$ was used. These salts, which are easily obtained in a perfectly pure condition, were reduced in a large flask by means of hydrochloric acid and alcohol. The chloride of silver thus formed was washed by decantation, dried, fused, and weighed without transfer. The united washings were supersaturated with ammonia, evaporated to dryness, and the residue treated with hot water. The resulting chromic oxide was then collected upon a filter, dried, ignited, and weighed. The results were as follows:

4.6680 grm. Ag_2CrO_4 gave	4.027 grm. AgCl and	1.0754 grm. Cr_2O_3.
3.4568 "	2.983 "	.7960 "
2.5060 "	2.1605 "	.5770 "
2.1530 "	1.8555 "	.4945 "
4.3335 grm. $Ag_2Cr_2O_7$ gave	2.8692 "	1.5300 "

From these weighings three values are calculable for the atomic weight of chromium. The three ratios upon which these values depend we will consider separately; taking first that between the chromic oxide and the original silver salt. In the four analyses of the normal chromate the percentages of Cr_2O_3 deducible from Berlin's weighings are as follows:

23.037
23.027
23.025
22.968

Mean, 23.014, $\pm$ .011

And from the single experiment with $Ag_2Cr_2O_7$ the percentage of Cr_2O_3 was 35.306.

For the ratio between Ag_2CrO_4 and AgCl, putting the latter at 100, we have for the former:

115.917
115.883
115.992
116.033

Mean, 115.956, $\pm$ .023

In the single experiment with anhydrochromate 100 AgCl is formed from 151.035 $Ag_2Cr_2O_7$.

Finally, for the ratio between AgCl and Cr_2O_3, the five experiments of Berlin give, for 100 parts of the former, the following quantities of the latter:

26.705
26.685
26.707
26.650
26.662

Mean, 26.682, ± .0076

These results will be discussed in connection with the work of other investigators at the end of this chapter.

In 1848 the researches of Moberg* appeared. His method simply consisted in the ignition of anhydrous chromic sulphate and of ammoniacal chrome alum, and the determination of the amount of chromic oxide thus left as residue. In the sulphate, $Cr_2(SO_4)_3$, the subjoined percentages of Cr_2O_3 were found. The brackets indicate two different samples of material, to which, however, we are justified in ascribing equal value:

.542	grm. sulphate gave	.212	grm. Cr_2O_3.	39.114	per cent.	}
1.337	"	.523	"	39.117	"	}
.5287	"	.207	"	39.153	"	}
1.033	"	.406	"	39.303	"	}
.868	"	.341	"	39.286	"	}

Mean, 39.1946, ± .0280

From the alum, $(NH_4)_2Cr_2(SO_4)_4.24H_2O$, we have these percentages of Cr_2O_3. The first series represents a salt long dried under a bell jar at a temperature of 18°. The crystals taken were clear and transparent, but may possibly have lost traces of water,† which would tend to increase the atomic weight found for chromium. In the second series the salt was carefully dried between folds of filter paper, and

* Journ. für Prakt. Chem., 43, 114.

† This objection is suggested by Berlin in a short note upon Lefort's paper. Journ. für Prakt. Chem., 71, 191.

results were obtained quite near those of Berlin. Both of these series are discussed together, neither having a remarkable value:

1.3185	grm. alum gave	.213	grm. Cr_2O_3.	16.155	per cent.	
.7987	"	.129	"	16.151	"	
1.0185	"	.1645	"	16.151	"	
1.0206	"	.1650	"	16.167	"	
.8765	"	.1420	"	16.201	"	
.7680	"	.1242	"	16.172	"	
1.6720	"	.2707	"	16.190	"	
.5410	"	.0875	"	16.174	"	
1.2010	"	.1940	"	16.153	"	
1.0010	"	.1620	"	16.184	"	
.7715	"	.1235	"	16.007	"	
1.374	"	.2200	"	16.012	"	

Mean, 16.143, ± .0125

The determinations made by Lefort* are even less valuable than those by Moberg. This chemist started out from pure barium chromate, which, to thoroughly free it from moisture, had been dried for several hours at 250°. The chromate was dissolved in pure nitric acid, the barium thrown down by sulphuric acid, and the precipitate collected upon a filter, dried, ignited, and weighed in the usual manner. The natural objection to the process is that traces of chromium may be carried down with the sulphate, thus increasing its weight. In fact, Lefort's results are somewhat too high. Calculated from his weighings, 100 parts of $BaSO_4$ correspond to the amounts of $BaCrO_4$ given in the third column:

1.2615	grm. $BaCrO_4$ gave	1.1555	grm. $BaSO_4$.	109.174
1.5895	"	1.4580	"	109.019
2.3255	"	2.1340	"	108.974
3.0390	"	2.7855	"	109.101
2.3480	"	2.1590	"	108.754
1.4230	"	1.3060	"	108.708
1.1975	"	1.1005	"	108.814
3.4580	"	3.1690	"	109.119
2.0130	"	1.8430	"	109.224

* Journ. für Prakt. Chem., 51, 261. 1850.

3.5570 grm. $BaCrO_4$ gave	3.2710 grm. $BaSO_4$.			108.744
1.6470	"	1.5060	"	109.363
1.8240	"	1.6725	"	109.058
1.6950	"	1.5560	"	108.933
2.5960	"	2.3870	"	108.756

Mean, 108.9815, ± .0369

Wildenstein,* in 1853, also made barium chromate the basis of his researches. A known weight of pure barium chloride was precipitated by a neutral alkaline chromate, and the precipitate allowed to settle until the supernatant liquid was perfectly clear. The barium chromate was then collected on a filter, washed with hot water, dried, gently ignited, and weighed. Here again arises the objection that the precipitate may have retained traces of alkaline salts, and again we find deduced an atomic weight which is too high. One hundred parts $BaCrO_4$ correspond to $BaCl_2$ as follows:

81.87	81.57
81.80	81.75
81.61	81.66
81.78	81.83
81.52	81.66
81.84	81.80
81.85	81.66
81.70	81.85
81.68	81.57
81.54	81.83
81.66	81.71
81.55	81.63
81.81	81.56
81.86	81.58
81.54	81.67
81.68	81.84

Mean, 81.702, ± .014

Next in order we have to consider two papers by Kessler, who employed a peculiar volumetric method entirely his own. In brief, he compared the oxidizing power of potassium anhydrochromate with that of the chlorate, and from

* Journ. für Prakt. Chem., 59. 27.

his observations deduced the ratio between the molecular weights of the two salts.

In his earlier paper* the mode of procedure was about as follows: The two salts, weighed out in quantities having approximate chemical equivalency, were placed in two small flasks, and to each was added 100 cc. of a ferrous chloride solution and 30 cc. hydrochloric acid. The ferrous chloride was added in trifling excess, and, when action ceased, the amount unoxidized was determined by titration with a standard solution of anhydrochromate. As in each case the quantity of ferrous chloride was the same, it became easy to deduce from the data thus obtained the ratio in question. I have reduced all of his somewhat complicated figures to a simple common standard, and give below the amount of chromate equivalent to 100 of chlorate:

120.118
120.371
120.138
120.096
120.241
120.181
Mean, 120.191, ± .028

In his later paper† Kessler substituted arsenic trioxide for the iron solution. In one series of experiments the quantity of anhydrochromate needed to oxidize 100 parts of the arsenic trioxide was determined, and in another the latter substance was similarly compared with the chlorate. The subjoined columns give the quantity of each salt proportional to 100 of As_2O_3:

$K_2Cr_2O_7$.	$KClO_3$.
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
	41.199
Mean, 99.045, ± .028	41.224

* Poggend. Annal., 95, 208. 1855.

† Poggend. Annal., 113, 137. 1861.

	$KClO_3$.
	41.161
	41.193
	41.149
	41.126
Mean,	41.172, ± .009

From the data given in the earlier paper, if we use our recent values for chlorine, potassium, and oxygen,

	$K_2Cr_2O_7$	= 293.937, ± .086
And from the later,	"	= 294.159, ± .119
General mean,	"	= 294.013, ± .0697

Finally, we come to the determinations published by Siewert,* whose work does not seem to have attracted general attention. He, reviewing Berlin's work, found that upon reducing silver chromate with hydrochloric acid and alcohol, the chromic chloride solution always retained traces of silver chloride dissolved in it. These could be precipitated by dilution with water; but, in Berlin's process, they naturally came down with the chromium hydroxide, making the weight of the latter too high. Hence too large a value for the atomic weight of chromium. In order to find a more correct value Siewert resorted to the analysis of sublimed, violet, chromic chloride. This salt he fused with sodium carbonate and a little nitre, treated the fused mass with water, and precipitated from the resulting solution the chlorine by silver nitrate in presence of nitric acid. The weight of the silver chloride thus obtained, estimated after the usual manner, gave means for calculating the atomic weight of chromium. His figures, reduced to a common standard, give, as proportional to 100 parts of chloride of silver, the quantities of chromic chloride stated in the third of the subjoined columns:

* Zeitschrift Gesammt. Wissenschaften, 17, 530. 1861.

.2367 grm. Cr_2Cl_6 gave	.6396 grm. AgCl.			37.007
.2946	"	.7994	"	36.853
.2593	"	.7039	"	36.838
.4935	"	1.3395	"	36.842
.5850	"	1.5884	"	36.830
.6511	"	1.76681	"	36.852
.5503	"	1.49391	"	36.836

Mean, 36.865, ± .0158

The first of these figures varies so widely from the others that we are justified in rejecting it; in which case the mean becomes 36.842, ± .0031.

Siewert also made two analyses of silver anhydrochromate by the following process. The salt, dried at 120°, was dissolved in nitric acid. The silver was then thrown down by hydrochloric acid, and, in the filtrate, chromium hydroxide was precipitated by ammonia. Reduced to a uniform standard, we find from his results, corresponding to 100 parts of AgCl, $Ag_2Cr_2O_7$, as in the last column:

.7866 grm. $Ag_2Cr_2O_7$ gave	.52202 AgCl and	.2764 Cr_2O_3.	150.684
1.089 "	.72249 "	.3840 "	150.729

Mean, 150.706, ± .015

Giving Berlin's single estimation equal weight with one of these, and combining, we get a general mean of 150.816, ± .074.

Siewert's percentages of Cr_2O_3 obtained from $Ag_2Cr_2O_7$, are as follows, calculated from the above weighings.

35.139
35.262

Mean, 35.2005, ± .0415

Combining, as before, with Berlin's single result, giving the latter equal weight with one of these, we have a general mean of 35.236, ± .0335.

For the ratio between silver chloride and chromic oxide, Siewert's two analyses of the anhydrochromate come out as follows. For 100 parts of AgCl we have of Cr_2O_3:

52.948
53.150

Mean, 53.049, $\pm$ .068

This figure, reduced to the standard of Berlin's work on the monochromate, becomes 26.525, $\pm$ .034. Berlin's mean was 26.682, $\pm$ .0076. The two means, combined, give a general mean of 26.676, $\pm$ .074.

We may now consider the ratios before us, which are as follows:

(1.) Percentage Cr_2O_3 from Ag_2CrO_4, 23.014, $\pm$ .011
(2.) Percentage Cr_2O_3 from $Ag_2Cr_2O_7$, 35.236, $\pm$ .0335
(3.) $AgCl : Ag_2CrO_4$: : 100 : 115.956, $\pm$ .023
(4.) $AgCl : Ag_2Cr_2O_7$: : 100 : 150.816, $\pm$ .074
(5.) $AgCl : Cr_2O_3$: : 100 : 26.676, $\pm$ .0074
(6.) Percentage Cr_2O_3 in chromic sulphate, 39.1946, $\pm$ .0280
(7.) Percentage Cr_2O_3 in ammonia chrome alum, 16.143, $\pm$ .0125
(8.) $BaSO_4 : BaCrO_4$: : 100 : 108.9815, $\pm$ .0369
(9.) $BaCrO_4 : BaCl_2$: : 100 : 81.702, $\pm$ .014
(10.) Molecular weight of $K_2Cr_2O_7$, 294.013, $\pm$ .0697
(11.) $AgCl : CrCl_3$: : 100 : 36.842, $\pm$ .0031

From these ratios we can at once deduce five values for the molecular weight of Cr_2O_3, as follows:

From (1)	Cr_2O_3	= 152.612, $\pm$ .074
" (2)	"	= 151.905, $\pm$ .165
" (5)	"	= 152.634, $\pm$ .044
" (6)	"	= 154.464, $\pm$ .135
" (7)	"	= 154.512, $\pm$ .125
General mean	"	= 152.855, $\pm$ .034

For barium chromate we get two values:

From (8)	$BaCrO_4$	= 253.494, $\pm$ .094
" (9)	"	= 253.976, $\pm$ .067
General mean	"	= 253.816, $\pm$ .054

From (3) we get	Ag_2CrO_4	= 331.739, $\pm$ .070
" (4) "	$Ag_2Cr_2O_7$	= 431.470, $\pm$ .215
" (11) "	$CrCl_3$	= 158.102, $\pm$ .018

Finally, from these intermediate data we derive six values for the atomic weight of chromium:

From $BaCrO_4$	Cr	= 53.200,	± .064
" Cr_2O_3	"	= 52.482,	± .018
" Ag_2CrO_4	"	= 52.536,	± .074
" $Ag_2Cr_2O_7$	"	= 52.188,	± .109
" $K_2Cr_2O_7$	"	= 52.116,	± .078
" $CrCl_3$	"	= 51.992,	± .047
General mean	"	= 52.453,	± .015
Or, if O = 16	"	= 52.574	

On account of the wide discrepancies between different data, and of the known constant errors vitiating some of the series of experiments, the foregoing general mean can have but little real value. In fact, a careful consideration of all the work represented in it will show that the most accurate estimate of the atomic weight of chromium must be deduced from the experiments of either Berlin, Kessler, or Siewert. Berlin's figures, taken by themselves, and combined, give, if the single analysis of silver anhydrochromate be assigned equal weight with a single analysis in the monochromate series, Cr = 52.389, ± .019; or, if O = 16, Cr = 52.511.

Siewert's results, both for chromic chloride and the silver anhydrochromate, properly combined, give Cr = 52.009, ± .025. If O = 16, this value becomes Cr = 52.129. In brief, the atomic weight of chromium may be nearly 52.5, or it may be 52. Only a revision of all the experiments could enable us to decide positively between these values. But as Siewert has pointed out probable sources of error in Berlin's work, I am inclined to give preference to the lower value.

MANGANESE.

Rejecting the early experiments of J. Davy and of Arfvedson, the first determinations of the atomic weight of manganese which we encounter are those of Turner* and of Berzelius.† Both of these chemists used the same method.

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* Trans. Roy. Soc. Edin., 11, 143. 1831.

† Lehrbuch, 5th Ed., 3, 1224.

The chloride of manganese was fused in a current of dry hydrochloric acid, and subsequently precipitated with a solution of silver. From the subjoined weighings I calculate the ratio given in the third column between $MnCl_2$ and 100 parts of AgCl:

4.20775 grm. $MnCl_2$ =	9.575 grm. AgCl.	43.945	Berzelius.
3.063 " =	6.96912 "	43.950	Berzelius.
12.47 grains $MnCl_2$ =	28.42 grains AgCl.	43.878	—Turner.
	Mean,	43.924, ± .015	

Hence the molecular weight of $MnCl_2$ is 125.662, ± .045.

Many years later Dumas* also made the chloride of manganese the starting point of some atomic weight determinations. The salt was fused in a current of hydrochloric acid, and afterwards titrated with a standard solution of silver in the usual way. 100 parts of Ag are equivalent to the quantities of $MnCl_2$ given in the third column:

3.3672 grm. $MnCl_2$ =	5.774 grm. Ag.	58.317
3.0872 "	5.293 "	58.326
2.9671 "	5.0875 "	58.321
1.1244 "	1.928 "	58.320
1.3134 "	2.251 "	58.321
	Mean,	58.321, ± .001

Hence $MnCl_2$ = 125.594, ± .011. This, combined with Berzelius and Turner's figures, gives $MnCl_2$ = 125.598, ± .011. And Mn = 54.858, ± .031.

An entirely different method of investigation was followed by v. Hauer,† who, as in the case of cadmium, ignited the sulphate in a stream of sulphuretted hydrogen, and determined the quantity of sulphide thus formed. I subjoin his weighings, and also the percentage of MnS in $MnSO_4$ as calculated from them:

* Ann. Chem. Pharm., 113, 25. 1860.
† Journ. für Prakt. Chem., 72, 360. 1857.

4.0626 grm. $MnSO_4$ gave	2.3425 grm. MnS.	57.660 per cent.	
4.9367 "	2.8442 "	57.613 "	
5.2372 "	3.0192 "	57.649 "	
7.0047 "	4.0347 "	57.600 "	
4.9175 "	2.8297 "	57.543 "	
4.8546 "	2.7955 "	57.585 "	
4.9978 "	2.8799 "	57.625 "	
4.6737 "	2.6934 "	57.629 "	
4.7240 "	2.7197 "	57.572 "	
	Mean,	57.608, ± .008	

Hence Mn = 54.785, ± .031.

This method of v. Hauer's, which seemed to give good results with cadmium, is, according to Schneider,* inapplicable to manganese; for the reason that the sulphide of the latter metal is liable to be contaminated with traces of oxysulphide. Such an impurity would bring the atomic weight out too high. The results of two different processes, one carried out by himself and the other in his laboratory by Rawack, are given by Schneider in this paper.

Rawack reduced manganoso-manganic oxide to manganous oxide by ignition in a stream of hydrogen, and weighed the water thus formed. From his weighings I get the values in the third column, which represent the Mn_3O_4 equivalent to one gramme of water:

4.149 grm. Mn_3O_4 gave	0.330 grm. H_2O.	12.5727
4.649 "	.370 "	12.5643
6.8865 "	.5485 "	12.5552
7.356 "	.5855 "	12.5636
8.9445 "	.7135 "	12.5361
11.584 "	.9225 "	12.5572
	Mean,	12.5582, ± .0034

Hence Mn = 53.911, ± .026.

Here the most obvious source of error lies in the possible loss of water. Such a loss, however, would increase the apparent atomic weight of manganese; but we see that the value found is much lower than that obtained either by Dumas or v. Hauer.

* Poggend. Annal., 107, 605.

Schneider himself effected the combustion of manganous oxalate with oxide of copper. The salt was not absolutely dry, so that it was necessary to collect both water and carbon dioxide. Then, upon deducting the weight of water from that of the original material, the weight of anhydrous oxalate was easily ascertained. Subtracting from this the CO_2, we get the weight of Mn. If we put $CO_2 = 100$, the quantities of manganese equivalent to it will be found in the last column:

1.5075 grm. oxalate gave	.306 grm. H_2O and	.7445 grm. CO_2.	61.3835
2.253 "	.4555 "	1.1135 "	61.4291
3.1935 "	.652 "	1.5745 "	61.4163
5.073 "	1.028 "	2.507 "	61.3482
		Mean,	61.3943, ± .0122

Hence Mn = 53.904, ± .014.

This result agrees beautifully with the value calculated from Rawack's experiments.

Now to combine the four independent values which we have thus far obtained:

From $MnCl_2$	Mn	= 54.858, ± .031
" $MnSO_4$	"	= 54.785, ± .031
" Mn_3O_4	"	= 53.911, ± .026
" MnC_2O_4	"	= 53.904, ± .014
General mean	"	= 54.128, ± .011
If O = 16	"	= 54.251

The considerations already cited, however, go to show that this general mean must be slightly affected by some plus constant error. It is probable, therefore, that a more correct figure will result from rejecting the first and second values in the above combination, and taking the data furnished by Rawack and Schneider alone. Combining their figures, we get as follows. Mn = 53.906, ± .012. Or, if O = 16, Mn = 54.029.

Since the foregoing calculations were made Dewar and Scott* have reported the following experiments. From the

* Nature, Sept. 15, 1881, p. 470.

complete analysis of silver permanganate, putting Ag = 108 and O = 16, they find in three estimations Mn = 55.51, 54.04, and 54.45. From the analysis of pure MnO_2, made from the nitrate, Mn = 53.3 to 53.6. Up to the date of writing a detailed account of the methods employed has not been published.

IRON.

The atomic weight of iron has been determined almost exclusively from the composition of ferric oxide. Beyond this there are only a few comparatively unimportant experiments by Dumas relative to ferrous and ferric chlorides.

Most of the earlier data relative to the percentage of metal and oxygen in ferric oxide we may reject at once, as set aside by later investigations. Among this no longer valuable material there is a series of experiments by Berzelius, another by Döbereiner, and a third by Capitaine. The work done by Stromeyer and by Wackenroder was probably good, but I am unable to find its details. The former found 30.15 per cent. of oxygen in the oxide under consideration, while Wackenroder obtained figures ranging from a minimum of 30.01 to a maximum of 30.38 per cent.*

In 1844 Berzelius † published two determinations of the ratio in question. He oxidized iron by means of nitric acid, and weighed the oxide thus formed. He thus found that when O = 100 Fe = 350.27 and 350.369.

Hence the following percentages of Fe in Fe_2O_3.

70.018
70.022

Mean, 70.020, ± .0013

About the same time Svanberg and Norlin ‡ published

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* For additional details concerning these earlier papers I must refer to Oudemans' monograph, pp. 140, 141.

† Ann. Chem. Pharm., 50, 432. Berz. Jahresb., 25, 43.

‡ Berzelius' Jahresbericht, 25, 42.

two elaborate series of experiments; one relating to the synthesis of ferric oxide, the other to its reduction. In the first set pure piano-forte wire was oxidized by nitric acid, and the amount of oxide thus formed was determined. The results were as follows:

1.5257 grm.	Fe gave	2.1803 grm.	Fe_2O_3.	69.977	per cent. Fe.
2.4051	"	3.4390	"	69.936	"
2.3212	"	3.3194	"	69.928	"
2.32175	"	3.3183	"	69.968	"
2.2772	"	3.2550	"	69.960	"
2.4782	"	3.5418	"	69.970	"
2.3582	"	3.3720	"	69.935	"

Mean, 69.9534, ± .0050

In the second series ferric oxide was reduced by ignition in a current of hydrogen, yielding the subjoined percentages of metal:

2.98353 grm.	Fe_2O_3 gave	2.08915 grm.	Fe.	70.025	per cent.
2.41515	"	1.6910	"	70.015	"
2.99175	"	2.09455	"	70.014	"
3.5783	"	2.505925	"	70.030	"
4.1922	"	2.9375	"	70.072	"
3.1015	"	2.17275	"	70.056	"
2.6886	"	1.88305	"	70.036	"

Mean, 70.0354, ± .0055

It is evident that one or both of these series must be vitiated by constant errors, and that these probably arise from impurities in the materials employed. Impurities in the wire taken for the oxidation series could hardly have been altogether avoided, and in the reduction series it is possible that weighable traces of hydrogen may have been retained by the iron. At all events it is probable that the errors of both series are in contrary directions, and, therefore, in some measure compensatory.

In 1844 there was also published an important paper by Erdmann and Marchand.* These chemists prepared ferric oxide by the ignition of pure ferrous oxalate, and submitted

* Journ. für Prakt. Chem., 33, 1.

it to reduction in a stream of hydrogen. Two sets of results were obtained with two different samples of ferrous oxalate, prepared by two different methods. For present purposes, however, it is not necessary to discuss these sets separately. The percentages of iron in Fe_2O_3 come out as follows:

70.013	A.
69.962	A.
69.979	A.
70.030	A.
69.977	A.
70.044	B.
70.015	B.
70.055	B.

Mean, 70.0094, ± .0080

In 1850 Maumené's* results appeared. He dissolved pure iron wire in aqua regia, precipitated with ammonia, filtered off the precipitate, washed thoroughly, ignited, and weighed, after the usual methods of quantitative analysis. The percentages of Fe in Fe_2O_3 are given in the third column:

1.482 grm. Fe gave	2.117 grm. Fe_2O_3.	70.005 per cent.
1.452 "	2.074 "	70.010 "
1.3585 "	1.941 "	69.990 "
1.420 "	2.0285 "	70.002 "
1.492 "	2.1315 "	69.998 "
1.554 "	2.220 "	70.000 "

Mean, 70.0008, ± .0019

Two more results, obtained by Rivot† through the reduction of ferric oxide in hydrogen, remain to be noticed. The percentages are:

69.31
69.35

Mean, 69.33, ± .013

We have thus before us six series of results, which we may now combine.

* Compt. Rend., Oct. 17, 1850.
† Ann. Chem. Pharm., 78, 214. 1851.

Berzelius	70.020,	$\pm$ .0013
Erdmann and Marchand	70.0094,	$\pm$ .0080
Svanberg and Norlin, Oxyd.	69.9534,	$\pm$ .0050
" Reduc.	70.0354,	$\pm$ .0055
Maumené	70.0008,	$\pm$ .0019
Rivot	69.33,	$\pm$ .013
General mean	70.0075,	$\pm$ .0010

From this we get Fe = 55.891, $\pm$ .012; or, if O = 16, this becomes 56.0195.

Dumas'* results, obtained from the chlorides of iron, are of so little weight that they might safely be omitted from our present discussion. For the sake of completeness, however, we will include them.

Pure ferrous chloride, ignited in a stream of hydrochloric acid gas, was dissolved in water and titrated with a silver solution in the usual way. One hundred parts of silver are equivalent to the amounts of $FeCl_2$ given in the third column:

3.677 grm. $FeCl_2$	= 6.238 grm. Ag.	58.945
3.924 "	= 6.675 "	58.787
	Mean,	58.866, $\pm$ .053

Ferric chloride, titrated in the same way, gave these results:

1.179 grm. Fe_2Cl_6	= 2.3475 grm. Ag.	50.224
1.242 "	2.471 "	50.263
	Mean,	50.2435, $\pm$ .0132

These give us two additional values for Fe, as follows:

From $FeCl_2$	Fe = 56.028, $\pm$ .119
" Fe_2Cl_6	" = 56.189, $\pm$ .062

Combining these with the value deduced from the composition of Fe_2O_3, Fe = 55.891, $\pm$ .012, we get this general mean, Fe = 55.913, $\pm$ .012. If O = 16, this becomes Fe = 56.042.

* Ann. Chem. Pharm., 113, 26. 1860.

COPPER.

The atomic weight of copper has been chiefly determined from the composition of the black oxide and the anhydrous sulphate. In dealing with the first named compound all experimenters have agreed in reducing it with a current of hydrogen, and weighing the metal thus set free.

The earliest experiments of any value were those of Berzelius,* whose results were as follows:

7.68075 grm. CuO lost	1.55 grm. O.	79.820 per cent. Cu in CuO.
9.6115 "	1.939 "	79.826 " "
	Mean,	79.823, ± .002

Erdmann and Marchand,† who come next in chronological order, corrected their results for weighing in air. Their weighings, thus corrected, give us the subjoined percentages of metal in CuO:

63.8962 grm. CuO gave	51.0391 grm. Cu.	79.878 per cent.
65.1590 "	52.0363 "	79.860 "
60.2878 "	48.1540 "	79.874 "
46.2700 "	36.9449 "	79.846 "
	Mean,	79.8645, ± .0038

Still later we find a few analyses by Millon and Commaille.‡ These chemists not only reduced the oxide by hydrogen, but they also weighed, in addition to the metallic copper, the water formed in the experiments. In three determinations the results were as follows:

6.7145 grm. CuO gave	5.3565 grm. Cu and	1.5325 grm. H_2O.	79.775 per cent.
3.3945 "	2.7085 "	.7680 "	79.791 "
2.7880 "	2.2240 grm. Cu.		79.770 "
		Mean,	79.7787, ± .0043

For the third of these analyses the water estimation was not made, but for the other two it yielded results which, in

* Poggend. Annal., 8, 177.

† Journ. für Prakt. Chem., 31, 389. 1844.

‡ Fresenius' Zeitschrift, 2, 475. 1863.

the mean, would make the atomic weight of copper 63.087, $\pm$ .222. This figure has so high a probable error that we need not consider it further.

The results obtained by Dumas* are wholly unavailable. Indeed, he does not even publish them in detail. He merely says that he reduced copper oxide, and also effected the synthesis of the subsulphide, but without getting figures which were wholly concordant. He puts Cu = 63.5.

Latest of all, and probably the best also, we have the determinations by Hampe.† First, he attempted to estimate the atomic weight of copper by the quantity of silver which the pure metal could precipitate from its solutions. This attempt failed to give satisfactory results, and he fell back upon the old method of reducing the oxide. From ten to twenty grammes of material were taken in each experiment, and the weights were reduced to a vacuum standard:

20.3260 grm. CuO gave	16.2279 grm. Cu.	79.838 per cent.	
20.68851 "	16.51669 "	79.835 "	
10.10793 "	8.06926 "	79.831 "	
		Mean, 79.8347,	$\pm$ .0013

Hampe also determined the quantity of copper in the anhydrous sulphate, $CuSO_4$. From 40 to 45 grammes of the salt were taken at a time, the metal was thrown down by electrolysis, and the weights were all corrected. I subjoin the results:

40.40300 grm. $CuSO_4$ gave	16.04958 grm. Cu.	39.724 per cent.	
44.64280 "	17.73466 "	39.726 "	
		Mean, 39.725,	$\pm$ .0007

We now have four series of experiments upon copper oxide, as follows:

Berzelius	79.823,	$\pm$ .0020
Erdmann and Marchand	79.8645,	$\pm$ .0038
Millon and Commaille	79.7787,	$\pm$ .0043
Hampe	79.8347,	$\pm$ .0013
General mean	79.830,	$\pm$ .0010

* Ann. d. Chim. et Phys., (3.) 55, 129.
† Fresenius' Zeitschrift, 13, 352.

For copper we have—

From composition of CuO	Cu	= 63.181,	± .036
" $CuSO_4$, (Hampe)	"	= 63.171,	± .012
General mean	"	= 63.173,	± .011

If O = 16, then Cu becomes = 63.318.

The close agreement between the two independent values for Cu is certainly very striking. It will be seen that Hampe's two estimates upon the sulphate carry (perhaps accidentally) much greater weight than all the experiments upon the oxide. This might seem like giving them undue credit, were it not for the fact of the remarkable concordance of the results above referred to. Either estimate for Cu would be valid without the other.

MOLYBDENUM.

If we leave out of account the inaccurate determination made by Berzelius,* we shall find that the data for the atomic weight of molybdenum lead to two independent estimates of its value; one near 92, the other near 96. The earlier results found by Berlin and by Svanberg and Struve lead to the lower number; the more recent work of Debray, Dumas, and Lothar Meyer sustains the higher. The latter value is the more probable, although both may be vitiated by constant errors in opposite directions.

The earliest investigation which we need especially to consider is that of Svanberg and Struve.† These chemists tried a variety of different methods, but finally based their conclusions upon the two following: first, molybdenum trioxide was fused with potassium carbonate, and the carbon dioxide which was expelled was estimated; secondly, molybdenum disulphide was converted into the trioxide by

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* Poggend. Annal., 8, 1. 1826.

† Journ. für Prakt. Chem., 44, 301. 1848.

roasting, and the ratio between the weights of the two substances was determined.

By the first method it was found that 100 parts of MoO_3 will expel the following quantities of CO_2:

31.4954
31.3749
31.4705

Mean, 31.4469, ± .0248

The carbon dioxide was determined simply from the loss of weight when the weighed quantities of trioxide and carbonate were fused together. It is plain that if, under these circumstances, a little of the trioxide should be volatilized, the total loss of weight would be slightly increased. A constant error of this kind would tend to bring out the atomic weight of molybdenum too low.

By the second method, the conversion by roasting of MoS_2 into MoO_3, Svanberg and Struve obtained these results. Two samples of artificial disulphide were taken, A and B, and yielded for each hundred parts the following of trioxide:

89.7919	A.
89.7291	A.
89.6436	B.
89.7082	B.
89.7660	B.
89.7640	B.
89.8635	B.

Mean, 89.7523, ± .0176

Three other experiments in series B gave divergent results, and, although published, are rejected by the authors themselves. Hence it is not necessary to cite them in this discussion. We again encounter in these figures the same source of constant error which apparently vitiates the preceding series, namely, the possible volatilization of the trioxide. Here, also, such an error would tend to reduce the atomic weight of molybdenum.

Upon discussing the data given in the foregoing para-

graphs we get somewhat noticeable results. From the carbon dioxide series, Mo = 91.711, ± .113, a figure having no unusual interest. From the other series, if S = 31.987 and O = 15.9633, we get Mo = 92.979, ± .354; but if we take S = 32 and O = 16, then Mo becomes = 92.133. In this case the higher values for oxygen and sulphur lead to a lower number for molybdenum. In the carbonate series the assumption of 12 and 16 for C and O, respectively, makes Mo = 92.033. In other words, if we assume the ordinary even numbers for C, O, and S, Svanberg and Struve's two methods yield more nearly concordant results than when the revised values for these elements are taken.

Berlin,* a little later than Svanberg and Struve, determined the atomic weight of molybdenum by igniting a molybdate of ammonium and weighing the residual MoO_3. Here, again, a loss of the latter by volatilization may (and probably does) lead to too low a result. The salt used was $(NH_4)_4Mo_5O_{17}.3H_2O$, and in it these percentages of MoO_3 were found:

81.598
81.612
81.558
81.555

Mean, 81.581, ± .0095

Hence Mo = 91.9817, ± .0776; a result agreeing quite well with those of Svanberg and Struve.

Until 1859 the value 92 was generally accepted on the basis of the foregoing researches, but in this year Dumas† published some figures tending to sustain a higher number. He prepared molybdenum trioxide by roasting the disulphide, and then reduced it to metal by ignition in hydrogen. At the beginning the hydrogen was allowed to act at a comparatively low temperature, in order to avoid volatilization of trioxide; but at the end of the operation the heat

* Journ. für Prakt. Chem., 49, 444. 1850.
† Ann. Chem. Pharm., 105, 84, and 113, 23.

was raised sufficiently to insure a complete reduction. From the weighings I calculate the percentages of metal in MoO_3:

.448 grm. MoO_3 gave	.299 grm. Mo.	66.741 per cent.
.484 "	.323 "	66.736 "
.484 "	.322 "	66.529 "
.498 "	.332 "	66.667 "
.559 "	.373 "	66.726 "
.388 "	.258 "	66.495 "

Mean, 66.649, ± .030

In 1868 the same method was employed by Debray.* His trioxide was purified by sublimation in a platinum tube. His percentages are as follows:

5.514 grm. MoO_3 gave	3.667 grm. Mo.	66.503 per cent.
7.910 "	5.265 "	66.561 "
9.031 "	6.015 "	66.604 "

Mean, 66.556, ± .020

This mean, combined with that of Dumas', gives a general mean of 66.585, ± .017.

Hence Mo = 95.429, ± .057.

Debray also made two experiments upon the precipitation of molybdenum trioxide in ammoniacal solution by nitrate of silver. In his results, as published, there is curious discrepancy, which, I have no doubt, is due to typographical error. These results I am, therefore, compelled to leave out of consideration. They could not, however, exert a very profound influence upon the final discussion.

The most recent investigation upon the atomic weight of molybdenum is the discussion by Lothar Meyer† of the experimental results obtained by Liechti and Kemp‡ in their analyses of the chlorides. Of these compounds there are four: $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. The chlorine in each was estimated as silver chloride, and the molybdenum as disulphide. From these analyses Meyer deduces three

* Compt. Rend., 66, 734.

† Ann. Chem. Pharm., 169, 365. 1873.

‡ Ann. Chem. Pharm., 169, 344.

sets of ratios, namely: between $MoCl_n$ and n AgCl; between $MoCl_n$ and MoS_2, and between MoS_2 and n AgCl. We will use only the first and last of these; the probable error of the atomic weight deduced from the second being relatively so high as to make the value connected with it comparatively unimportant. The analyses of the trichloride, being discordant, are here rejected.

By reducing the weighings published by Liechti and Kemp* to a common standard we get the following percentage results. In $MoCl_2$ the subjoined quantities of the original substance and of MoS_2 correspond to 100 parts of AgCl:

$MoCl_2$.	*MoS_2.*
58.299	55.762
58.194	55.591
58.524	56.065
Mean, 58.339, ± .066	Mean, 55.806, ± .093

Hence $MoCl_2$ = 166.902, ± .188, and MoS_2 = 159.652, ± .268.

With the tetrachloride similarly calculated we get these figures, corresponding to 100 parts AgCl:

$MoCl_4$.	*MoS_2.*
41.492	27.957
41.319	
Mean, 41.4055, ± .0583	

Hence $MoCl_4$ = 236.914, ± .358, and MoS_2, if given the weight of a single experiment in the dichloride series, = 159.964, ± .627.

* These are as follows:

.2666 grm. $MoCl_2$ gave	.2550	grm. MoS_2 and	.4573	grm. AgCl.
.1811 "	.1730	"	.3112	"
.2530 "	.2422	"	.4320	"
.4126 grm. $MoCl_4$ gave	.2780	"	.9944	"
.1923 "	——	"	.4654	"
.5810 grm. $MoCl_5$ gave	.3414	"	1.5222	"
.2466 "	.1441	"	.6465	"

For the pentachloride the following quantities balance 100 of AgCl:

$MoCl_5$.	MoS_2.
38.168	22.428
38.057	22.289
Mean, 38.112, ± .038	Mean, 22.3585, ± .040

Hence $MoCl_5$ = 272.587, ± .271, and MoS_2 = 159.914, ± .287.

We have now the molecular weight of each chloride, and three values for that of the disulphide. Combining the latter we get a general mean, as follows:

From $MoCl_2$ series	MoS_2	= 159.652, ± .268
" $MoCl_4$ "	"	= 159.964, ± .627
" $MoCl_5$ "	"	= 159.914, ± .287
General mean	"	= 159.790, ± .187

With these data, in addition to those given by Dumas and by Debray, we get five estimates of the atomic weight of molybdenum:

Dumas and Debray's data	Mo	= 95.429, ± .057
From molecular weight of $MoCl_2$	"	= 96.262, ± .190
" " $MoCl_4$	"	= 95.434, ± .363
" " $MoCl_5$	"	= 95.737, ± .280
" " MoS_2	"	= 95.816, ± .188
General mean	"	= 95.527, ± .051

Or, if O = 16, Mo = 95.747.

It will at once be seen that the most reliable results are those obtained by the reduction of molybdenum trioxide. Traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weight. Our final figure, therefore, may be a trifle too high, but the early value, 92, is unquestionably very far too low.

Since the foregoing discussion was written a single experiment by Rammelsberg * has been brought to my notice.

* Berlin Monatsbericht, 1877, 574.

Closely following Dumas' method, he reduced molybdenum trioxide to metal, finding in it 66.708 per cent. of the latter. This figure comes within the limits of variation of Dumas' experiments, and therefore gives them additional confirmation. Its introduction into the general mean, however, would exert too little influence upon the latter to justify the labor of recalculation.

TUNGSTEN.

The atomic weight of tungsten has been determined from analyses of the trioxide, the hexchloride, and the tungstates of iron, silver, and barium.

The composition of the trioxide has been the subject of many investigations. Malaguti * reduced this substance to the blue oxide, and from the difference between the weights of the two compounds obtained a result now known to be considerably too high. In general, however, the method of investigation has been to reduce WO_3 to W in a stream of hydrogen at a white heat, and afterwards to reoxidize the metal, thus getting from one sample of material two results for the percentage of tungsten. This method is unquestionably accurate, provided that the trioxide used be pure.

The first experiments which we need consider are, as usual, those of Berzelius.† 899 parts WO_3 gave, on reduction, 716 of metal. 676 of metal, reoxidized, gave 846 WO_3. Hence these percentages of W in WO_3:

79.644, by reduction.
79.905, by oxidation.

Mean, 79.7745, $\pm$ .0880

These figures are far too high, the error being undoubtedly due to the presence of alkaline impurity in the trioxide employed.

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* Journ. für Prakt. Chem., 8, 179. 1836.
† Poggend. Annal., 8, 1. 1826.

Next in order of time comes the work of Schneider,* who, with characteristic carefulness, took every precaution to get pure material. His percentages of tungsten are as follows:

Reduction Series.

79.336
79.254
79.312
79.326
79.350

Mean, 79.3156, ± .0112

Oxidation Series.

79.329
79.324
79.328

Mean, 79.327, ± .0010

Closely agreeing with these figures are those of Marchand,† published in the following year:

Reduction Series.

79.307
79.302

Mean, 79.3045, .0017

Oxidation Series.

79.321
79.352

Mean, 79.3365, ± .0105

The figures obtained by v. Borch‡ agree in mean tolerably well with the foregoing. They are as follows:

Reduction Series.

79.310
79.212
79.289
79.313
79.225
79.290
79.302

Mean, 79.277, ± .0106

* Journ. für Prakt. Chem., 50, 152. 1850.
† Ann. Chem. Pharm., 77, 261. 1851.
‡ Journ. für Prakt. Chem., 54, 254. 1851.

Oxidation Series.

79.359
79.339

Mean, 79.349, ± .0067

Dumas* gives only a reduction series, based upon trioxide obtained by the ignition of a pure ammonium tungsten. The reduction was effected in a porcelain boat, platinum being objectionable on account of the tendency of tungstate to alloy with it. Dumas publishes only weighings, from which I have calculated the percentages:

2.784	grm. WO_3 gave	2.208	grm. W.	79.310	per cent.
2.994	"	2.373	"	79.259	"
4.600	"	3.649	"	79.326	"
.985	"	.781	"	79.289	"
.917	"	.727	"	79.280	"
.917	"	.728	"	79.389	"
1.717	"	1.362	"	79.324	"
2.988	"	2.370	"	79.317	"
			Mean,	79.312, ± .009	

The data furnished by Bernoulli† differ widely from those just given. This chemist undoubtedly worked with impure material, the trioxide having a greenish tinge. Hence the results are too high. These are the percentages of W:

Reduction Series.

79.556
79.526
79.553
79.558
79.549
78.736

Mean, 79.413, ± .091

Oxidation Series.

79.558
79.656
79.555
79.554

Mean, 79.581, ± .017

* Ann. Chem. Pharm., 113, 23. 1860.
† Poggend. Annal., 111, 573. 1860.

Two reduction experiments by Persoz * give the following results:

1.7999 grm. WO_3 gave	1.4274 grm. W.		79.304 per cent.
2.249	"	1.784	"	79.324 "
			Mean,	79.314, ± .007

Finally, we have the work done by Roscoe.† This chemist used a porcelain boat and tube, and made six weighings, after successive reductions and oxidations, with the same sample of 7.884 grammes of trioxide. These weighings give me the following five percentages, which, for the sake of uniformity with foregoing series, I have classified under the usual, separate headings:

Reduction Series.

79.196
79.285
79.308

Mean, 79.263, ± .023

Oxidation Series.

79.230
79.299

Mean, 79.2645, ± .0233

There are still other experiments by Riche,‡ which I have not been able to get in detail. They cannot be of any value, however, for they give to tungsten an atomic weight of about ten units too low. We may therefore neglect this series, and go on to combine the others:

Berzelius	79.7745,	± .088
Schneider, Reduction	79.3156,	± .0112
" Oxidation	79.327,	± .0010
Marchand, Reduction	79.3045,	± .0017
" Oxidation	79.3365,	± .0105
v. Borch, Reduction	79.277,	± .0106
" Oxidation	79.349,	± .0067

* Zeit. Anal. Chem., 3, 260. 1864.
† Ann. Chem. Pharm., 162, 368. 1872.
‡ Journ. für Prakt. Chem., 69, 10. 1857.

Dumas	79.312,	± .009
Bernouilli, Reduction	79.413,	± .091
" Oxidation	79.581,	± .017
Persoz	79.314,	± .007
Roscoe, Reduction	79.263,	± .023
" Oxidation	79.2645,	± .0233
General mean	79.3215,	± .00085

The rejection of the figures given by Berzelius and by Bernoulli exerts an unimportant influence upon the final result. There is, therefore, no practical objection to retaining them in the discussion.

In 1861 Scheibler* deduced the atomic weight of tungsten from analyses of barium metatungstate, $BaO.4WO_3.9H_2O$. In four experiments he estimated the barium as sulphate, getting closely concordant results, which were, however, very far too low. These, therefore, are rejected. But from the percentage of water in the salt a very good result was attained. The percentages of water are as follows:

13.053
13.054
13.045
13.010
13.022

Mean, 13.0368, ± .0060

The work of Zettnow,† published in 1867, was somewhat more complicated than any of the foregoing researches. He prepared the pure tungstates of silver and of iron, and from their composition determined the atomic weight of tungsten.

In the case of the iron salt the method of working was this: The pure, artificial $FeWO_4$ was fused with sodium carbonate, the resulting sodium tungstate was extracted by water, and the thoroughly washed, residual ferric oxide was dissolved in hydrochloric acid. This solution was then reduced by zinc, and titrated for iron with potassium permanganate. Corrections were applied for the drop in excess of

* Journ. für Prakt. Chem., 83, 324.
† Poggend. Annal., 130, 30.

permanganate needed to produce distinct reddening, and for the iron contained in the zinc. 11.956 grammes of the latter metal contained iron corresponding to 0.6 cc. of the standard solution. The permanganate was standardized by comparison with pure ammonium-ferrous sulphate, $Am_2Fe(SO_4)_2 . 6 H_2O$, so that, in point of fact, Zettnow establishes directly only the ratio between that salt and the ferrous tungstate. From Zettnow's four experiments in standardizing I find that 1 cc. of his solution corresponds to 0.0365457 grammes of the double sulphate, with a probable error of $\pm$ .0000012.

Three sets of titrations were made. In the first a quantity of ferrous tungstate was treated according to the process given above; the iron solution was diluted to 500 cc., and four titrations made upon 100 cc. at a time. The second set was like the first, except that three titrations were made with 100 cc. each, and a fourth upon 150 cc. In the third set the iron solution was diluted to 300 cc., and only two titrations upon 100 cc. each were made. In sets one and two thirty grammes of zinc were used for the reduction of each, while in number three but twenty grammes were taken. Zettnow's figures, as given by him, are quite complicated; therefore I have reduced them to a common standard. After applying all corrections the following quantities of tungstate, in grammes, correspond to 1 cc. of permanganate solution:

.028301	First set.
.028291	
.028311	
.028301	
.028367	Second set.
.028368	
.028367	
.028367	
.028438	Third set.
.028438	

Mean, .0283549, $\pm$ .0000115

With the silver tungstate, Ag_2WO_4, Zettnow employed two methods. In two experiments the substance was de-

composed by nitric acid, and the silver thus taken into solution was titrated with standard sodium chloride. In three others the tungstate was treated directly with common salt, and the residual silver chloride collected and weighed. Here again, on account of some complexity in Zettnow's figures, I am compelled to reduce his data to a common standard. To 100 parts of AgCl the following quantities of Ag_2WO_4 correspond:

By First Method.

161.665
161.603

Mean, 161.634, ± .021

By Second Method.

161.687
161.651
161.613

Mean, 161.650, ± .014

General mean from both series, 161.645, ± .012

Finally, we have two analyses by Roscoe of tungsten hexchloride, published in the same paper with his results upon the trioxide. In one experiment the chlorine was determined as AgCl; in the other the chloride was reduced by hydrogen, and the residual tungsten estimated. By bringing both results into one form of expression we have for the percentage of chlorine in WCl_6:*

53.588
53.632

Mean, 53.610, ± .015

We have now five ratios from which to calculate the atomic weight of tungsten:

(1.) Percentage of W in WO_3, 79.3215, ± .00085
(2.) Percentage of H_2O in $BaO.4WO_3.9H_2O$, 13.0368, ± .0060

* The actual figures are as follows:

19.5700 grm. WCl_6 gave 42.4127 grm. AgCl.
10.4326 " 4.8374 " tungsten.

(3.) $Am_2Fe(SO_4)_2.6H_2O$: $FeWO_4$: : .0365457, ± .0000012 : .0283549, ± .0000115

(4.) AgCl : Ag_2WO_4 : : 100 : 161.645, ± .012

(5.) Percentage of Cl in WCl_6, 53.610, ± .015

From these we get five values for tungsten, as follows:

From	(1)	W =	183.703, ± .041
"	(2)	" =	183.532, ± .156
"	(3)	" =	183.923, ± .120
"	(4)	" =	183.248, ± .069
"	(5)	" =	183.639, ± .109
	General mean	" =	183.610, ± .032
	Or, if O = 16, then	" =	184.032

URANIUM.

It is not the purpose of the present investigation to examine at all systematically such questions as are involved in the discussion whether the atomic weight of uranium is 120 or 240. For convenience we may use the formulæ based upon the smaller number, and, if eventually the larger value proves to be correct, it will be easy to double the figures which we obtain. Suffice it to say here, that the specific heat of the green oxide, according to Donath,* agrees best with the formula U_3O_4 and the lower atomic weight. On the other hand, the value 240 fits best into such schemes as that given by Mendelejeff in his paper on the periodic law. An accurate determination of the specific heat of the metal itself is much needed, for the material with which Regnault worked was of uncertain quality; furthermore, the vapor density of some volatile uranium compounds ought to be ascertained.† Until some such data have been rigidly

* Ber. d. Deutsch. Chem. Gesell., 12, 742. 1879.

† The value of 240 for uranium is strongly sustained by the recent experiments of Zimmermann upon the vapor density of the tetrachlorid and tetrabromid. For UBr_4 the vapor density is 19.46, while theory (U = 240) requires 19.36. For UCl_4 the v. d. 13.33 was found. Theory, 13.21. (Ber. der Deutsch. Chem. Gesell., 14, s. 1934. 1881.)

established the controversy over the two rival values can hardly be satisfactorily settled.

The earlier attempts to determine the atomic weight of uranium were all vitiated by the erroneous supposition that the uranous oxide was really the metal. The supposition, of course, does not affect the weighings and analytical data which were obtained, although these, from their discordance with each other and with later and better results, have now only a historical value.

For present purposes the determinations made by Berzelius,* by Arfvedson,† and by Marchand,‡ may be left quite out of account. Berzelius employed various methods, while the others relied upon estimating the percentage of oxygen lost upon the reduction of U_3O_4 to UO. Rammelsberg's || results also, although very suggestive, need no full discussion. He analyzed the green chloride, UCl_2; effected the synthesis of uranyl sulphate from uranous oxide; determined the amount of residue left upon the ignition of the sodio and bario-uranic acetates; estimated the quantity of magnesium uranate formed from a known weight of UO, and attempted also to fix the ratio between the green and the black oxides. His figures vary so widely that they could count for little in the establishing of any general mean; and, moreover, they lead to estimates of the atomic weight which are mostly below the true value. For instance, twelve lots of U_3O_4 from several different sources were reduced to UO by heating in hydrogen. The percentages of loss varied from 3.83 to 4.67, the mean being 4.121. These figures give values for the atomic weight of uranium ranging from 92.66 to 117.65, or, in mean, 107.50. Such discordance is due partly to impurity in some of the material studied, and illustrates the difficulties inherent in the problem to be solved. Some of the uranoso-uranic oxide was prepared by

* Schweigg. Journ., 22, 336. 1818. Poggend. Annal., 1, 359. 1825.

† Poggend. Annal., 1, 245. Berz. Jahr., 3, 120. 1822.

‡ Journ. für Prakt. Chem., 23, 497. 1841.

|| Poggend. Annal., 55, 318, 1842; 56, 125, 1842; 59, 9, 1843; 66, 91, 1845. Journ. für Prakt. Chem., 29, 324.

calcining the oxalate, and retained an admixture of carbon. Many such points were worked up by Rammelsberg with much care, so that his papers should be scrupulously studied by any chemist who contemplates a redetermination of the atomic weight of uranium.

In 1841 and 1842 Peligot published certain papers* showing that the atomic weight of uranium must be somewhere near 120. A few years later the same chemist published fuller data concerning the constant in question, but in the time intervening between his earlier and his final researches other determinations were made by Ebelmen and by Wertheim. These investigations we may properly discuss in chronological order. For present purposes the early work of Peligot may be dismissed as only preliminary in character. It showed that what had been previously regarded as metallic uranium was in reality an oxide, but gave figures for the atomic weight of the metal which were merely approximations.

Ebelmen's† determinations of the atomic weight of uranium were based upon analyses of uranic oxalate. This salt was dried at 100°, and then, in weighed amount, ignited in hydrogen. The residual uranous oxide was weighed, and in some cases converted into U_3O_4 by heating in oxygen. The following weights are reduced to a vacuum standard:

10.1644 grm. oxalate gave	7.2939 grm. UO.				
12.9985	"	9.3312	"	Gain on oxidation,	.3685
11.8007	"	8.4690	"	"	.3275
9.9923	"	7.1731	"	"	.2812
11.0887	"	7.9610	"	"	.3105
10.0830	"	7.2389	"		
6.7940	"	4.8766	"		
16.0594	"	11.5290	"	"	.4531

Reducing these figures to percentages, we may present the results in two columns. Column A gives the percentages of UO in the oxalate, while B represents the amount of U_3O_4 formed from 100 parts of UO:

* Compt. Rend., 12, 735. 1841. Ann. Chim. Phys., (3,) 55. 1842.
† Journ. für Prakt. Chem., 27, 385. 1842.

A.	B.
71.924	------
71.787	103.949
71.767	103.867
71.621	103.920
71.794	103.900
71.793	------
71.778	------
71.790	103.930
Mean, 71.782, ± .019	Mean, 103.913, ± .009

From column A, the molecular weight of UO = 134.523, ± .102
" B, " " = 135.985, ± .326

General mean .... UO = 134.652, ± .097

From column A .... U = 118.560
" B .... " = 120.022
From general mean of both columns .. " = 118.689, ± .097

Wertheim's* experiments were even simpler in character than those of Ebelmen. Sodio-uranic acetate, carefully dried at 200°, was ignited, leaving the following percentages of sodium uranate:

67.51508
67.54558
67.50927

Mean, 67.52331, ± .0076

Hence the molecular weight of $Na_2U_4O_7$ = 634.865, ± .191. And U = 119.282, ± .048.

The final results of Peligot's† investigations appeared in 1846. Both the oxalate and the acetate of uranium were studied and subjected to combustion analysis. The oxalate was scrupulously purified by repeated crystallizations, and thirteen analyses, representing different fractions, were made. Seven of these gave imperfect results, due to incomplete purification of the material; six only, from the later crystallizations, need to be considered. In these the uranium

* Journ. für Prakt. Chem., 29, 209. 1843.
† Compt. Rend., 22, 487.

was weighed as U_3O_4, and the carbon as CO_2. From the ratio between the CO_2 and U_3O_4 the atomic weight of uranium may be calculated without involving any error due to traces of moisture possibly present in the oxalate. I subjoin Peligot's weighings, and give, in the third column, the U_3O_4 proportional to 100 parts of CO_2:

CO_2.	U_3O_4.	Ratio.
1.456 grm.	4.649 grm.	319.299
1.369 "	4.412 "	322.279
2.209 "	7.084 "	320.688
1.019 "	3.279 "	321.786
1.069 "	3.447 "	322.461
1.052 "	3.389 "	322.148
		Mean, 321.443, ± .338

Hence $U_3O_4 = 423.342, \pm .451$.

From the acetate, $C_2H_3(UO)O_2.H_2O$, the following percentages of U_3O_4 were obtained:

5.061 grm. acetate gave	3.354 grm. U_3O_4.	66.2715 per cent.
4.601 "	3.057 "	66.4421 "
1.869 "	1.238 "	66.2386 "
3.817 "	2.541 "	66.5706 "
10.182 "	6.757 "	66.3622 "
4.393 "	2.920 "	66.4694 "
2.868 "	1.897 "	66.1437 "
		Mean, 66.3569, ± .038

The acetate also yielded the subjoined percentages of carbon and of water. Assuming that the figures for carbon were calculated from known weights of dioxide, with $C = 12$ and $O = 16$, I have added a third column, in which the carbon percentages are converted into percentages of CO_2:

H_2O.	C.	CO_2.
21.60	11.27	41.323
21.16	11.30	41.433
21.10	11.30	41.433
21.20	11.10	40.700
Mean, 21.265, ± .187	11.24	41.222, ± .092

From all of these figures we may calculate the molecular weight of the uranic acetate as follows:

From percentage of U_3O_4	$C_2H_3(UO)O_2.H_2O$	= 212.629, ±	.242
" CO_2	"	= 212.999, ±	.476
" H_2O	"	= 211.184, ±	1.863
General mean	"	= 212.685, ±	.214

We have now before us the molecular weights of four uranium compounds, giving us four values for U:

(1.) UO = 134.652, ± .097 .... Ebelmen.
(2.) $Na_2U_4O_7$ = 634.865, ± .191 .... Wertheim.
(3.) U_3O_4 = 423.342, ± .451 .... Peligot.
(4.) $C_2H_3(UO)O_2.H_2O$ = 212.685, ± .214 . "

The four values for uranium combine as follows:

From (1)	U = 118.689, ± .097	Ebelmen.
" (2)	" = 119.282, ± .048	Wertheim.
" (3)	" = 119.830, ± .150	Peligot.
" (4)	" = 119.885, ± .215	"
General mean	" = 119.241, ± .041	

Or, if O = 16, U = 119.515, or 239.030.

Considering Peligot's figures by themselves, and combining values 3 and 4, we have U = 119.849, ± .123; or, if O = 16, U = 120.125, or 240.250.

It is plain that the atomic weight of uranium needs to be scrupulously revised. The foregoing figures are by no means satisfactory. Chemically considered, it is probable that Peligot's work is the best, and that his results should be given preference. His figures from the oxalate and the acetate tally well with each other, whereas Ebelmen's two sets of results vary widely. From the percentage of UO yielded by the oxalate, Ebelmen's figures give a low value for U. From his oxidation of UO to U_3O_4 we get a value nearly two units higher. Peligot, in his work with the oxalate, found it, even after three or four crystallizations, to be contaminated with oxalic acid, and rejected the figures obtained from impure material. Probably Ebelmen's low values are due to the same impurity.

ALUMINUM.

The atomic weight of aluminum has been determined by Berzelius, Mather, Tissier, Dumas, Isnard, Terreil, and Mallet. The early calculations of Davy and of Thomson we may properly disregard.

Berzelius'* determination rests upon a single experiment. He ignited 10 grammes of dry aluminum sulphate, $Al_2(SO_4)_3$, and obtained 2.9934 grammes of Al_2O_3 as residue. Hence, if S = 31.987 and O = 15.9633, Al = 27.243.

In 1835† Mather published a single analysis of aluminum chloride, from which he sought to fix the atomic weight of the metal. 0.646 grm. of Al_2Cl_6 gave him 2.056 of AgCl and 0.2975 of Al_2O_3. These figures give worthless values for Al, and are included here only for the sake of completeness. From the ratio between AgCl and Al_2Cl_6, Al = 28.925.

Tissier's‡ determination, also resting on a single experiment, appeared in 1858. Metallic aluminum, containing .135 per cent. of sodium, was dissolved in hydrochloric acid. The solution was evaporated with nitric acid to expel all chlorine, and the residue was strongly ignited until only alumina remained. 1.935 grm. of Al gave 3.645 grm of Al_2O_3. If we correct for the trace of sodium in the aluminum, we have Al = 27.073.

Essentially the same method of determination was adopted by Isnard,|| who, although not next in chronological order, may fittingly be mentioned here. He found that 9 grm. of aluminum gave 27 grm. of Al_2O_3. Hence Al = 26.938.

In 1858 Dumas,§ in connection with his celebrated revision of the atomic weights, made seven experiments with aluminum chloride. The material was prepared in quantity,

* Poggend. Annal., 8, 177.

† Silliman's Amer. Journ., 27, 241.

‡ Compt. Rend., 46, 1105.

|| Compt. Rend., 66, 508. 1868.

§ Ann. Chim. Phys., (3,) 55, 151. Ann. Chem. Pharm., 113, 26.

sublimed over iron filings, and finally resublimed from metallic aluminum. Each sample used was collected in a small glass tube, after sublimation from aluminum in a a stream of dry hydrogen, and hermetically enclosed. Having been weighed in the tube, it was dissolved in water, and the quantity of silver necessary for precipitating the chlorine was determined. Reducing to a common standard, his weighings give the quantities of Al_2Cl_6 stated in the third column, as proportional to 100 parts of silver:

1.8786 grm. Al_2Cl_6	=	4.543 grm. Ag.		41.352
3.021	"	7.292	"	41.459—Bad.
2.399	"	5.802	"	41.348
1.922	"	4.6525	"	41.311
1.697	"	4.1015	"	41.375
4.3165	"	10.448	"	41.314
6.728	"	16.265	"	41.365

In the second experiment the Al_2Cl_6 contained traces of iron. Rejecting this experiment the remaining six give a mean of 41.344, ± .007. Hence Al = 27.441, ± .082.

In consequence of these figures of Dumas, the atomic weight of aluminum has generally of late years been put at 27.5, and the lower results deduced from the work of other investigators have been disregarded.

In 1879 Terreil* published a new determination of the atomic weight under consideration, based upon a direct comparison of the metal with hydrogen. Metallic aluminum, contained in a tube of hard glass, was heated strongly in a current of dry hydrochloric acid. Hydrogen was set free, and was collected over a strong solution of caustic potash. 0.410 grm. of aluminum thus were found equivalent to 508.2 cc., or .0455 grm. of hydrogen. Hence Al = 27.033.

About a year after Terreil's determination appeared the lower value for aluminum was thoroughly confirmed by J. W. Mallet.† After giving a full resumé of the work done by others, exclusive of Isnard, the author describes his own experiments, which may be summarized as follows:

* Bulletin de la Soc. Chimique, 31, 153.

† Phil. Trans., 1880, p. 1003.

Four methods of determination were employed, each one simple and direct, and at the same time independent of the others. First, pure ammonia alum was calcined, and the residue of aluminum oxide was estimated. Second, aluminum bromide was titrated with a standard solution of silver. Third, metallic aluminum was attacked by caustic soda, and the hydrogen evolved was measured. Fourth, hydrogen was set free by aluminum, and weighed as water. Every weight was carefully verified, the verification being based upon the direct comparison, by J. E. Hilgard, of a kilogramme weight with the standard kilogramme at Washington. The specific gravity of each piece was determined, and also of all materials and vessels used in the weighings. During each weighing both barometer and thermometer were observed, so that every result represents a real weight *in vacuo*.

The ammonium alum used in the first series of experiments was specially prepared, and was absolutely free from ascertainable impurities. The salt was found, however, to lose traces of water at ordinary temperatures; a circumstance which tended towards a slight elevation of the apparent atomic weight of aluminum as calculated from the weighings. Two sets of experiments were made with the alum; one upon a sample air-dried for two hours at 21°–25°, the other upon material dried for twenty-four hours at 19°–26°. These sets, marked A and B respectively, differ slightly; B being the less trustworthy of the two, judged from a chemical standpoint. Mathematically it is the better of the two. Calcination was effected with a great variety of precautions, concerning which the original memoir must be consulted. To Mallet's weighings I append the percentages of Al_2O_3 deduced from them:

Series A.

8.2144 grm. of the alum gave	.9258 grm. Al_2O_3.		11.270 per cent.
14.0378	"	1.5825	"	11.273 "
5.6201	"	.6337	"	11.275 "
11.2227	"	1.2657	"	11.278 "
10.8435	"	1.2216	"	11.266 "

Mean, 11.2724, ± .0014

Series B.

12.1023	grm. of the alum gave	1.3660	grm. Al_2O_3.	11.287	per cent.
10.4544	"	1.1796	"	11.283	"
6.7962	"	.7670	"	11.286	"
8.5601	"	.9654	"	11.278	"
4.8992	"	.5528	"	11.283	"
			Mean,	11.2834,	$\pm$ .0011

Combined, these series give a general mean of 11.2793, $\pm$ .0008. Hence Al = 27.075, $\pm$ .011.

The aluminum bromide used in the second series of experiments was prepared by the direct action of bromine upon the metal. The product was repeatedly distilled, the earlier portions of each distillate being rejected, until a constant boiling point of 263.°3 at 747 mm. pressure was noted. The last distillation was effected in an atmosphere of pure nitrogen, in order to avoid the possible formation of oxide or oxy-bromide of aluminum; and the distillate was collected in three portions, which proved to be sensibly identical. The individual samples of bromide were collected in thin glass tubes, which were hermetically sealed after nearly filling. For the titration pure silver was prepared, and after fusion upon charcoal it was heated in a Sprengel vacuum in order to eliminate occluded gases. This silver was dissolved in specially purified nitric acid, the latter but very slightly in excess. The aluminum bromide, weighed in the sealed tube, was dissolved in water, precautions being taken to avoid any loss by splashing or fuming which might result from the violence of the action. To the solution thus obtained the silver solution was added, the silver being something less than a decigramme in deficiency. The remaining amount of silver needed to complete the precipitation of the bromine was added from a burette, in the form of a standard solution containing one milligramme of metal to each cubic centimetre. The final results were as follows, the figures in the third column representing the quantities of bromide proportional to 100 parts of silver. Series A is from the first portion of the last distillate of Al_2Br_6; series

B from the second portion, and series C from the third portion:

Series A.		
6.0024 grm. Al_2Br_6	= 7.2793 grm. Ag.	82.458
8.6492 "	10.4897 "	82.454
3.1808 "	3.8573 "	82.462
Series B.		
6.9617 "	8.4429 "	82.456
11.2041 "	13.5897 "	82.445
3.7621 "	4.5624 "	82.459
5.2842 "	6.4085 "	82.456
9.7338 "	11.8047 "	82.457
Series C.		
9.3515 "	11.3424 "	82.447
4.4426 "	5.3877 "	82.458
5.2750 "	6.3975 "	82.454

Mean, 82.455, ± .001

Hence Al = 27.046, ± .061.

The high probable error of this result is due to the high probable error of the atomic weight of bromine.

The experiments to determine the amount of hydrogen evolved by the action of caustic soda upon metallic aluminum were conducted with pure metal, specially prepared, and with caustic soda made from sodium. The soda solution was so strong as to scarcely lose a perceptible amount of water by the passage through it of a dry gas at ordinary temperature. As the details of the experiments are somewhat complex, the original memoir must be consulted for them. The following results were obtained, the weight of the hydrogen being calculated from the volume, by Regnault's data corrected for the latitude and elevation of the University of Virginia:

Weight of Al.	*Vol. of H.*	*Wt. of H.*	*At. Wt.*
.3697 grm.	458.8 c. c.	.04106 grm.	27.012
.3769 "	467.9 "	.04187 "	27.005
.3620 "	449.1 "	.04019 "	27.022
.7579 "	941.5 "	.08425 "	26.998
.7314 "	907.9 "	.08125 "	27.006
.7541 "	936.4 "	.08380 "	26.996

Mean, 27.005, ± .0032

The closing series of experiments was made with larger quantities of aluminum than were used in the foregoing set. The hydrogen, evolved by the action of the caustic alkali, was dried by passing it through two drying tubes containing pumice stone and sulphuric acid, and two others containing asbestos and phosphorus pentoxide. Thence it passed through a combustion tube containing copper oxide heated to redness. A stream of dry nitrogen was employed to sweep the last traces of hydrogen into the combustion tube, and dry air was afterwards passed through the entire apparatus to reoxidize the surface of reduced copper, and to prevent the retention of occluded hydrogen. The water formed by the oxidation of the hydrogen was collected in three drying tubes. The results obtained were as follows. The third column gives the amount of water formed from 10 grammes of aluminum:

2.1704 grm. Al gave	2.1661 grm. H_2O.	9.9802
2.9355 "	2.9292 "	9.9785
5.2632 "	5.2562 "	9.9867
	Mean,	9.9818, $\pm$ .0017

Hence Al = 26.998, $\pm$ .007.

In combining the various determinations of the atomic weight of aluminum into one general mean, we must arbitrarily assign weight to the single experiments of Berzelius, Isnard, Tissier, and Terreil. This may fairly be done by giving to each the probable error, and therefore the weight, of a single observation in Dumas' series. Mather's work may be ignored altogether:

From Berzelius	Al =	27.243,	$\pm$ .201
" Tissier	" =	27.096,	$\pm$ .201
" Isnard	" =	26.938,	$\pm$ .201
" Dumas	" =	27.441,	$\pm$ .082
" Terreil	" =	27.033,	$\pm$ .201
" Mallet's alum experiments	" =	27.075,	$\pm$ .011
" " Al_2Br_6 "	" =	27.046,	$\pm$ .061
" " H "	" =	27.005,	$\pm$ .003
" " H_2O "	" =	26.998,	$\pm$ .007
General mean	" =	27.0092,	$\pm$ .0028

If O = 16, Al = 27.075. Taking Mallet's work alone, Al = 27.0089, ± .0028.

Evidently all the data except Mallet's might be rejected without affecting sensibly the final result. Dumas' work is clearly vitiated by constant errors, but the determinations by Isnard, Tissier, and Terreil may be regarded as having some confirmative value.

GOLD.

The only determinations of the atomic weight of gold which are worthy of consideration are those of Berzelius and of Levol.

The earliest method adopted by Berzelius* was that of precipitating a solution of gold chloride by means of a weighed quantity of metallic mercury. The weight of gold thus thrown down gave the ratio between the atomic weights of the two metals. In the single experiment which Berzelius publishes, 142.9 parts of Hg precipitated 93.55 of Au. Hence, using the value for mercury given in a preceding chapter, 199.712, Au = 196.113.

In a later investigation† Berzelius resorted to the analysis of potassio-auric chloride, $2KCl.AuCl_3$. Weighed quantities of this salt were ignited in hydrogen; the resulting gold and potassium chloride were separated by means of water, and both were collected and estimated. The loss of weight upon ignition was, of course, chlorine. As the salt could not be perfectly dried without loss of chlorine, the atomic weight under investigation must be determined by the ratio between the KCl and the Au. If we reduce to a common standard, and compare with 100 parts of KCl, the equivalent amounts of gold will be those which I give in the last of the subjoined columns:

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* Poggend. Annal., 8, 177.

† Lehrbuch, 5 Aufl., 3, 1212.

4.1445 grm. K_2AuCl_5 gave	.8185 grm. KCl and	2.159 grm. Au.	263.775
2.2495 "	.44425 "	1.172 "	263.815
5.1300 "	1.01375 "	2.67225 "	263.600
3.4130 "	.674 "	1.77725 "	263.687
4.19975 "	.8295 "	2.188 "	263.773
			Mean, 263.730, $\pm$ .026

Hence Au = 196.186, $\pm$ .101.

Still a third series of experiments by Berzelius* may be included here. In order to establish the atomic weight of phosphorus he employed that substance to precipitate gold from a solution of gold chloride in excess. Between the weight of phosphorus taken and the weight of gold obtained it was easy to fix a ratio. Since the atomic weight of phosphorus has been better established by other methods, we may properly reverse this ratio and apply it to our discussion of gold. 100 parts of P precipitate the quantities of Au given in the third column:

.829 grm. P precipitated	8.714 grm. Au.	1051.15
.754 "	7.930 "	1051.73
		Mean, 1051.44, $\pm$ .196

Hence Au = 195.303, $\pm$ .589.

Levol's† estimation of the atomic weight under consideration can hardly have much value. A weighed quantity of gold was converted in a flask into $AuCl_3$. This was reduced by a stream of sulphur dioxide, and the resulting sulphuric acid was determined as $BaSO_4$. One gramme of gold gave 1.782 grm. $BaSO_4$. Hence Au = 195.794.

If we give this single experiment and Berzelius' single result with mercury each equal weight with one analysis in the potassio-auric chloride series, and include respectively the probable errors appertaining to Hg and to $BaSO_4$, we may combine all the data as follows:

* Lehrbuch, 5 Aufl., 3, 1188.

† Ann. d. Chim. et d. Phys., (3,) 30, 355. 1850.

From KCl : Au ratio	Au = 196.186,	± .101
From Hg : Au ratio	" = 196.113,	± .335
From P : Au ratio	" = 195.303,	± .589
From $BaSO_4$: Au ratio	" = 195.794,	± 1.234
General mean	" = 196.155,	± .095

Or, if O = 16, Au = 196.606.

As gold is a metal which can be readily applied to the determination of the atomic weights of other elements, an experimental revision of its atomic weight is very desirable.

NICKEL AND COBALT.

On account of the close similarity of these metals to each other, their atomic weights, approximately if not actually identical, have received of late years much attention.

The first determinations, and the only ones up to 1852, were made by Rothhoff;* each with but a single experiment. For nickel 188 parts of the monoxide were dissolved in hydrochloric acid; the solution was evaporated to dryness, the residue was dissolved in water, and precipitated by silver nitrate. 718.2 parts of silver chloride were thus formed; whence Ni = 58.925. The same process was applied also to cobalt, 269.2 parts of the oxide being found equivalent to 1029.9 of AgCl. Hence Co = 58.817. These values are so nearly equal that their differences were naturally ascribable to experimental errors. They are, however, entitled to no special weight at present, since it cannot be certain from any evidence recorded that the oxide of either metal was absolutely free from traces of the other.

In 1852 Erdmann and Marchand† published some results, but without details, concerning the atomic weight of nickel. They reduced the oxide by heating in a current of

* Cited by Berzelius. Poggend. Annal., 8, 184. 1826.

† Journ. für Prakt. Chem., 55, 202. 1852.

hydrogen, and obtained values ranging from 58.2 to 58.6, when O = 16. Their results were not very concordant, and the lowest was probably the best.

In 1856, incidentally to other work, Deville* found that 100 parts of pure metallic nickel yielded 262 of sulphate; whence Ni = 59.15.

To none of the foregoing estimations can any importance now be attached. The modern discussion of the atomic weights under consideration began with the researches of Schneider† in 1857. This chemist examined the oxalates of both metals, determining carbon by the combustion of the salts with copper oxide in a stream of dry air. The carbon dioxide thus formed was collected as usual in a potash bulb, which, in weighing, was counterpoised by a similar bulb, so as to eliminate errors due to the hygroscopic character of the glass. The metal in each oxalate was estimated, first by ignition in a stream of dry air, followed by intense heating in hydrogen. Pure nickel or cobalt was left behind in good condition for weighing. Four analyses of each oxalate were made, with the results given below. The nickel salt contained three molecules of water, and the cobalt salt two molecules:

$NiC_2O_4.3H_2O.$

1.1945	grm. gave	.528	grm. CO_2.	44.203 per cent.
2.5555	"	1.12625	"	44.072 "
3.199	"	1.408	"	44.014 "
5.020	"	2.214	"	44.104 "

Mean, 44.098, ± .027

The following percentages of nickel were found in this salt:

29.107
29.082
29.066
29.082

Mean, 29.084, ± .006

* Ann. Chim. Phys., (3,) 46, 182. 1856.
† Poggend. Annal., 101, 387. 1857.

$CoC_2O_4.2H_2O.$

1.6355 grm. gave	.781 grm. CO_2.		47.753 per cent.
1.107 "	.5295 "		47.832 "
2.309 "	1.101 "		47.683 "
3.007 "	1.435 "		47.722 "
		Mean,	47.7475, ± .0213

The following were the percentages found for cobalt:

32.552
32.619
32.528
32.523

Mean, 32.5555, ± .0149

In a later paper* Schneider also gives some results obtained with a nickel oxalate containing but two molecules of water. This gave him 47.605 per cent. of CO_2, and the following percentages of nickel:

31.4115
31.4038

Mean, 31.4076, ± .0026

The conclusion at which Schneider arrived was, that the atomic weights of cobalt and nickel are not identical, being about 60 and 58 respectively. The percentages given above will be discussed at the end of this chapter in connection with all the other data relative to the constants in question.

The next chemist to take up the discussion of these atomic weights was Marignac, in 1857.† His original paper is not accessible to me, and I am therefore obliged to give only such features of it as I can get from abstracts and reviews. He worked with the chlorides and sulphates of nickel and cobalt, using apparently common gravimetric methods. The sulphates, taken as anhydrous, were first ignited to expel $SO_2 + O$, after which the residues were heated with weighed amounts of lead silicate. The increase in weight

* Poggend. Annal., 107. 616.

† Jahresbericht, 1857, 225. Bibl. Univ. de Genève, (nouv. s.,) 1, 373.

was CoO or NiO respectively. The anhydrous chlorides were prepared from the hydrated salts by ignition in dry chlorine or hydrochloric acid. With cobalt, the monohydrated chloride, dried at 100°, was also employed. For nickel he gives the following values, referred probably to O = 16, S = 32, Ag = 108, Cl = 35.5:

From $NiSO_4$	Ni = 58.4 to 59.0
" $NiCl_2$	" = 58.4 " 59.28

To cobalt these values are assigned:

From $CoSO_4$	Co = 58.64 to 58.76
" $CoCl_2.H_2O$	" = 58.84 " 59.02
" $CoCl_2$	" = 58.72 " 59.02

That is, contrary to Schneider's view, the two atomic weights are approximately the same. The values for nickel, however, run a little lower than those for cobalt; a fact which is probably not without significance. Marignac criticizes Schneider's earlier paper, holding that the nickel oxalate may have contained some free oxalic acid, and that the cobalt salt was possibly contaminated with carbonate or with basic compounds. In his later papers Schneider rejects these suggestions as unfounded, and in turn criticizes Marignac. The purity of anhydrous $NiSO_4$ is not easy to guarantee, and, according to Schneider, the anhydrous chlorides of cobalt and nickel are liable to be contaminated with oxides. This is the case even when the chlorides are heated in chlorine, unless the gas is carefully freed from all traces of air and moisture.

Dumas'* determinations of the two atomic weights were made with the chlorides of nickel and cobalt. The pure metals were dissolved in aqua regia, the solutions were repeatedly evaporated to dryness, and the residual chlorides were ignited in dry hydrochloric acid gas. The last two estimations in the nickel series were made upon $NiCl_2$ formed by heating the spongy metal in pure chlorine. In the third column I give the $NiCl_2$ or $CoCl_2$, equivalent to 100 parts of silver:

* Ann. Chem. Pharm., 113, 25. 1860.

.9123 grm. $NiCl_2$	=	1.515 grm. Ag.	60.218	
2.295	"	3.8115 "	60.212	
3.290	"	5.464 "	60.212	
1.830	"	3.041 "	60.178	
3.001	"	4.987 "	60.176	
		Mean,	60.1992,	$\pm$ .0062

2.352 grm. $CoCl_2$	=	3.9035 grm. Ag.	60.254	
4.210	"	6.990 "	60.229	
3.592	"	5.960 "	60.268	
2.492	"	4.1405 "	60.186	
4.2295	"	7.0255 "	60.202	
		Mean,	60.2278,	$\pm$ .011

These results give values for Co and Ni differing by less than a tenth of a unit; here, as elsewhere, the figure for Ni being a trifle the lower.

In 1863* the idea that nickel and cobalt have equal atomic weights was strengthened by the researches of Russell. He found that the black oxide of cobalt, by intense heating in an atmosphere of carbon dioxide, became converted into a brown monoxide of constant composition. The ordinary oxide of nickel, on the other hand, was shown to be convertible into a definite monoxide by simple heating over the blast lamp. The pure oxides of the two metals, thus obtained, were reduced by ignition in hydrogen, and their exact composition thus ascertained. Several samples of each oxide were taken, yielding the following percentages of metal:

NiO.	
78.597	1st sample.
78.584	
78.608	
78.581	2d sample.
78.589	
78.583	
78.616	3d sample.
78.590	
78.588	
78.590	4th sample.
78.594	
78.597	
78.588	
Mean of all, 78.593, $\pm$ .0018	

* Journ. Chem. Soc., (2,) 1, 51.

CoO.	
78.591	1st sample.
78.588	
78.550	
78.598	
78.614	
78.603	2d sample.
78.591	
78.591	
78.588	3d sample.
78.592	
78.597	4th sample.
78.598	
78.595	5th sample.
78.589	
78.596	

Mean of all, 78.592, ± .0023

These percentages are practically identical, and lead to essentially the same mean value for each atomic weight.

In a later paper Russell* confirmed the foregoing results by a different process. He dissolved metallic nickel and cobalt in hydrochloric acid and measured the hydrogen evolved. Thus the ratio between the metal and the ultimate standard was fixed without the intervention of any other element. About two-tenths of a gramme of metal, or less, was taken in each experiment. 100 parts by weight of Co or Ni give the following weights of H, calculated from the volume of the latter:

Ni.		*Co.*	
3.420	1st sample.	3.395	1st sample.
3.418		3.398	
3.416		3.397	
3.417		3.398	
3.412		3.403	2d sample.
3.415		3.401	
3.416		3.401	

* Journ. Chem. Soc., (2.) 7, 494. 1869.

Ni.		*Co.*	
3.398	2d sample.	3.404	3d sample.
3.409		3.405	
3.404		3.410	4th sample.
3.401	—3d sample.	3.407	
3.412	4th sample.	Mean of all, 3.4017, ± .0009	
3.408			
3.410			
Mean of all, 3.411, ± .001			

A glance at the tabulated discussion which closes this chapter will show that these figures agree well with each other, and well with those found from the analyses of the oxides. The probable errors assigned in the hydrogen series may be a little too low, since they ought to be modified by the probable error of the weight of a unit volume of hydrogen. So insignificant a correction may, however, be neglected.

Some time after the publication of Russell's first paper, but before the appearance of his second, some other investigations were made known. Of these the first was by Sommaruga,* whose results, obtained by novel methods, closely confirmed those of Schneider and antagonized those of Dumas, Marignac, and Russell. The atomic weight of nickel Sommaruga deduced from analyses of the nickel potassium sulphate, $K_2Ni(SO_4)_2.6H_2O$, which, dried at 100°, has a perfectly definite composition. In this salt the sulphuric acid was determined in the usual way as barium sulphate, a process to which there are obvious objections. In the third column are given the quantities of the nickel salt proportional to 100 parts of $BaSO_4$:

0.9798 grm.	gave	1.0462 grm. $BaSO_4$.		93.653
1.0537	"	1.1251	"	93.654
1.0802	"	1.1535	"	93.645
1.1865	"	1.2669	"	93.654
3.2100	"	3.4277	"	93.649
3.2124	"	3.4303	"	93.648
			Mean,	93.6505, ± .001

* Sitzungsb. Wien Akad., 54, 2 Abth., 50. 1866.

For cobalt Sommaruga used the purpureo cobalt chloride of Gibbs and Genth. This salt, dried at 110°, is anhydrous and stable. Heated hotter, $CoCl_2$ remains. The latter, ignited in hydrogen, yields metallic cobalt. In every experiment the preliminary heating must be carried on cautiously until ammoniacal fumes no longer appear:

.6656 grm.	gave	.1588 grm. Co.		23.858 per cent.
1.0918	"	.2600	"	23.814 "
.9058	"	.2160	"	23.846 "
1.5895	"	.3785	"	23.813 "
2.9167	"	.6957	"	23.847 "
1.8390	"	.4378	"	23.806 "
2.5010	"	.5968	"	23.808 "

Mean, 23.827, ± .006

Further along this series will be combined with a similar one by Lee. It may here be said that Sommaruga's paper was quickly followed by a critical essay from Schneider,* endorsing the former's work, and objecting to the results of Russell.

In 1867 still another new process for the estimation of these atomic weights was put forward by Winkler,† who determined the amount of gold which pure metallic nickel and cobalt could precipitate from a neutral solution of sodio-auric chloride. Experimentally, the method seems to be quite accurate; practically, it involves a knowledge of the defectively ascertained atomic weight of gold. In order to obtain pure cobalt Winkler prepared purpureo-cobalt chloride, which, having been four or five times recrystallized, was ignited in hydrogen. His nickel was repeatedly purified by precipitation with sodium hypochlorite. From material thus obtained pure nickel chloride was prepared, which, after sublimation in dry chlorine, was also reduced by hydrogen. 100 parts of gold are precipitated by the quantities of nickel and cobalt given in the third columns respectively. In the cobalt series I include one experiment

* Poggend. Annal., 130, 310.
† Zeit. Anal. Chem., 6, 18. 1867.

by Weselsky which was published by him in a paper presently to be cited:

.4360	grm. nickel precipitated	.9648	grm. gold.	45.191
.4367	"	.9666	"	45.179
.5189	"	1.1457	"	45.291
.6002	"	1.3286	"	45.175
			Mean,	45.209, ± .019

.5890	grm. cobalt precipitated	1.3045	grm. gold.	45.151
.3147	"	.6981	"	45.080
.5829	"	1.2913	"	45.141
.5111	"	1.1312	"	45.182
.5821	"	1.2848	"	45.307
.559	"	1.241	"	45.044—Weselsky.
			Mean,	45.151, ± .025

Weselsky's paper,* already cited, relates only to cobalt. He ignited the cobalticyanides of ammonium and of phenylammonium in hydrogen, and from the determinations of cobalt thus made deduced its atomic weight. His results are as follows:

.7575	grm. $(NH_4)_6Co_2Cy_{12}$ gave	.166	grm. Co.	21.914 per cent.
.5143	"	.113	"	21.972 "
			Mean,	21.943, ± .029

.8529	grm. $(C_6H_8N)_6Co_2Cy_{12}$ gave	.1010	grm. Co.	11.842 per cent.
.6112	"	.0723	"	11.829 "
.7140	"	.0850	"	11.905 "
.9420	"	.1120	"	11.890 "
			Mean,	11.8665, ± .0124

Finally, we come to the work done by Lee† in the laboratory of Wolcott Gibbs. Like Weselsky, Lee ignited certain cobalticyanides and nickelocyanides in hydrogen and determined the residual metal. The double cyanides chosen were those of strychnia and brucia; salts of very high molecular weight, in which the percentages of metal are relatively low. A series of experiments with purpureo-cobalt

* Ber. d. Deutsch. Chem. Gesell., 2, 592. 1868.
† Am. Journ. Sci. and Arts, (3.) 2, 44. 1871.

chloride was also carried out. In order to avoid admixture of carbon in the metallic residues, the salts were first ignited in air, and then in oxygen. Reduction by hydrogen followed. The salts were in each case covered by a porous septum of earthenware, through which the hydrogen diffused, and which served to prevent the mechanical carrying away of solid particles; furthermore, heat was applied from above. The results attained were very satisfactory, and assign to nickel and cobalt atomic weights varying from each other by about a unit; Ni being nearly 58, and Co about 59. The exact figures will appear later. The cobalt results agree remarkably well with those of Weselsky. The following are the percentages of metal found:

In brucia nickelocyanide. $Ni_3Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6.10H_2O$.

5.724
5.729
5.750
5.733
5.712
5.729

Mean, 5.7295, ± .0034

In strychnia nickelocyanide, $Ni_3Cy_{12}(C_{21}H_{22}N_2O_2)_6.H_6.8H_2O$.

6.607
6.613
6.589
6.607
6.561
6.595

Mean, 6.595, ± .005

In brucia cobalticyanide, $Co_2Cy_{12}(C_{23}H_{26}N_2O_4)_6.H_6.20H_2O$.

3.759
3.720
3.739
3.748
3.747
3.749

Mean, 3.7437, ± .0036

In strychnia cobalticyanide, $Co_2Cy_{12}(C_{21}H_{22}N_2O_2)_6 . H_6 . 8H_2O$.

4.583
4.596
4.554
4.564
4.577
4.549

Mean, 4.5705, ± .005

In purpureo-cobalt chloride, $Co_2(NH_3)_{10}Cl_6$.

23.575
23.587
23.586
23.579
23.569
23.581

Mean, 23.5795, ± .0019

The last series may be combined with Sommaruga's, thus:

Sommaruga	23.827, ± .006
Lee	23.5795, ± .0019
General mean	23.6045, ± .0018

In discussing the atomic weights of nickel and cobalt, we may ignore the work of Rothhoff, Erdmann and Marchand and Deville. That of Marignac must also be omitted, for want of sufficient data. For nickel we have the following ratios. The probable error assigned in No. 4, is that of a single experiment in No. 2:

(1.) Per cent. of Ni in $NiC_2O_4.3H_2O$, 29.084, ± .006
(2.) " CO_2 from " 44.098, ± .027
(3.) " Ni in $NiC_2O_4.2H_2O$, 31.4076, ± .0026
(4.) " CO_2 from " 47.605, ± .053
(5.) " Ni in NiO, 78.593, ± .0018
(6.) " " brucia nickelocyanide, 5.7295, ± .0034
(7.) " " strychnia " 6.595, ± .005
(8.) Ag : $NiCl_2$: : 100 : 60.1992, ± .0062
(9.) Ni : H : : 100 : 3.411, ± .001
(10.) Au : Ni : : 100 : 45.209, ± .019
(11.) $BaSO_4$: $K_2Ni(SO_4)_2.6H_2O$: : 100 : 93.6505, ± .001

Since the proportion of water in the oxalates is not an absolutely certain quantity, the data concerning such salts

are best handled by employing the ratios between the carbon dioxide and the metal. Accordingly ratios (1) and (2) give a single value for Ni, and ratios (3) and (4) another. In all, we have nine values for the atomic weight in question:

From (1) and (2)	Ni	= 57.907, ± .0379
" (3) " (4)	"	= 57.926, ± .0654
" (6)	"	= 57.884, ± .0396
" (7)	"	= 57.947, ± .0467
" (11)	"	= 58.170, ± .0829
" (5)	"	= 58.607, ± .0139
" (9)	"	= 58.634, ± .0165
" (8)	"	= 58.899, ± .0339
" (10)	"	= 59.120, ± .0376
General mean	"	= 58.547, ± .0089

If O = 16, Ni = 58.682.

In the foregoing result it will be seen that the two sets of figures due to Russell receive very great weight. This is because the one set is referred directly to hydrogen, without the intervention of the probable error of any other element; while the second set involves only the atomic weight of oxygen, of which the probable error is small. As regards accuracy of methods, however, and certainty concerning the purity of material, Russell's work is no better than Schneider's, and probably inferior to Lee's. Now values one to five in the above table represent the tolerably concordant results of Schneider, Lee, and Sommaruga. They, combined by themselves, give a general mean of Ni = 57.928, ± .0215; or, if O = 16, of Ni = 58.062. This value, taking everything into account, I cannot but regard as more likely to prove correct than the larger mean deduced from all the ratios. At all events, the atomic weight of nickel needs further careful investigation.

For cobalt these ratios are available:

(1.) Per cent. of Co in $CoC_2O_4.2H_2O$, 32.5555, ± .0149
(2.) " CO_2 from " 47.7475, ± .0213
(3.) " Co in CoO, 78.592, ± .0023
(4.) " " purpureo-cobalt chloride, 23.6045, ± .0018
(5.) " " phenylammonium cobalticyanide, 11.8665, ± .0124
(6.) " " ammonium " 21.943, ± .029

(7.) Per cent. of Co in brucia cobalticyanide, 3.7437, ± .0036
(8.) " " strychnia " 4.5705, ± .005
(9.) Ag : $CoCl_2$: : 100 : 60.2278, ± .011
(10.) Co : H : : 100 : 3.4017, ± .0009
(11.) Au : Co : : 100 : 45.151, ± .025

Hence we have ten values for Co, as follows:

From	(1) and (2)	Co	= 59.865, ± .0394
"	(4)	"	= 59.080, ± .0152
"	(5)	"	= 58.913, ± .0628
"	(6)	"	= 59.177, ± .0816
"	(7)	"	= 59.057, ± .0581
"	(8)	"	= 58.960, ± .0708
"	(11)	"	= 59.044, ± .0436
"	(9)	"	= 58.961, ± .0392
"	(3)	"	= 58.604, ± .0145
"	(10)	"	= 58.794, ± .0162
	General mean	"	= 58.887, ± .008

If O = 16, Co = 59.023.

SELENIUM.

The atomic weight of this element was first determined by Berzelius,* who, saturating 100 parts of selenium with chlorine, found that 179 of chloride were produced. Further on these figures will be combined with similar results by Dumas.

We may omit, as unimportant for present purposes, the analyses of alkaline selenates made by Mitscherlich and Nitzsch,† and pass on to the experiments published by Sacc‡ in 1847. This chemist resorted to a variety of methods, some of which gave good results, while others were unsatisfactory. First, he sought to establish the exact composition of SeO_2, both by synthesis and by analysis. The former plan, according to which he oxidized pure selenium by

* Poggend. Annal., 8, 1. 1826.
† Poggend. Annal., 9, 623. 1827.
‡ Ann. d. Chim. et d. Phys., (3,) 21, 119.

nitric acid, gave poor results; better figures were obtained upon reducing SeO_2 with ammonium bisulphite and hydrochloric acid, and determining the percentage of selenium set free:

.6800 grm. SeO_2 gave	.4828 grm. Se.		71.000 per cent.	
3.5227 "	2.5047 "		71.102 "	
4.4870 "	3.1930 "		71.161 "	
		Mean,	71.088,	± .032

In a similar manner Sacc also reduced barium selenite, and weighed the resulting mixture of barium sulphate and free selenium. This process gave discordant results, and a better method was found in calcining $BaSeO_3$ with sulphuric acid, and estimating the resulting quantity of $BaSO_4$. In the third column I give the amounts of $BaSO_4$ equivalent to 100 of $BaSeO_3$:

.5573 grm. $BaSeO_3$ gave	.4929 grm. $BaSO_4$.		88.444	
.9942 "	.8797 "		88.383	
.2351 "	.2080 "		88.473	
.9747 "	.8621 "		88.448	
		Mean,	88.437,	± .013

Still other experiments were made with the selenites of silver and lead; but the figures were subject to such errors that they need no further discussion here.

A few years after Sacc's work was published, Erdmann and Marchand made with their usual care a series of experiments upon the atomic weight under consideration.* They alalyzed pure mercuric selenide, which had been repeatedly sublimed and was well crystallized. Their method of manipulation has already been described in the chapter upon mercury. These percentages of Hg in HgSe were found:

71.726
71.731
71.741

Mean, 71.7327, ± .003

* Journ. für Prakt. Chem., 55, 202. 1852.

The next determinations were made by Dumas,* who returned to the original method of Berzelius. Pure selenium was converted by dry chlorine into $SeCl_4$, and from the gain in weight the ratio between Se and Cl was easily deducible. I include Berzelius' single experiment, which I have already cited, and give in a third column the quantity of chlorine absorbed by 100 parts of selenium:

1.709 grm. Se absorb	3.049 grm. Cl.		178.409
1.810 "	3.219 "		177.845
1.679 "	3.003 "		178.856
1.498 "	2.688 "		179.439
1.944 "	3.468 "		178.395
1.887 "	3.382 "		179.226
1.935 "	3.452 "		178.398
			179.000—Berzelius.
		Mean,	178.696, ± .125

The question may here be properly asked, whether it would be possible thus to form $SeCl_4$ and be certain of its absolute purity? A trace of oxychloride, if simultaneously formed, would increase the apparent atomic weight of selenium. In point of fact, this method gives a higher value for Se than any of the other processes which have been adopted, and that value has the largest probable error of any one in the entire series. A glance at the table which summarizes the discussion at the end of this chapter will render this point sufficiently clear.

Latest of all, we come to the determinations made by Ekman and Pettersson.* They tried various methods of investigation, and finally decided upon the two following:

First. Pure silver selenite, Ag_2SeO_3 was ignited, leaving behind metallic silver in the subjoined percentages:

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* Ann. Chem. Pharm., 113, 32. 1860.

† Ber. d. Deutsch. Chem. Gesell., 9, 1210. 1876. Published in detail by the society at Upsala.

62.93
62.95
62.97
62.94
62.98
62.98
62.95

Mean, 62.957, ± .005

Second. A warm aqueous solution of selenious acid was mixed with HCl, and reduced by a current of SO_2. The reduced Se was collected upon a glass filter, dried, and weighed. Percentages of Se in SeO_2:

71.199
71.185
71.193
71.187
71.191

Mean, 71.191, ± .0016

This series, combined with that of Sacc, 71.088, ± .032, gives a general mean of 71.1907, ± .0016.

There are now five series of figures from which to deduce the atomic weight of selenium:

(1.) Per cent. of Se in SeO_2, 71.1907, ± .0016
(2.) $BaSeO_3 : BaSO_4 :: 100 : 88.437$, ± .013
(3.) Per cent. of Hg in HgSe, 71.7327, ± .003
(4.) $Se : SeCl_4 :: 100 : 178.696$, ± .125
(5.) Per cent. of Ag in Ag_2SeO_3, 62.957, ± .005

From these we get the following values for selenium:

From (1)	Se	= 78.894, ± .018
" (2)	"	= 78.362, ± .053
" (3)	"	= 78.700, ± .019
" (4)	"	= 79.174, ± .064
" (5)	"	= 78.819, ± .025
General mean	"	= 78.797, ± .011

If O = 16, Se = 78.978.

TELLURIUM.

Particular interest attaches to the atomic weight of tellurium, on account of the speculations of Mendelejeff. According to the "periodic law" of that chemist, tellurium should lie between antimony and iodine, having an atomic weight greater than 120, and less than 127. Theoretically, Mendelejeff assigns it a value of Te = 125; but all the published determinations lead to a mean number higher than would be admissible under the aforesaid "periodic law." Whether theory or experiment is at fault remains to be discovered.

The first, and for many years the only, determinations of the constant in question, were made by Berzelius.* By means of nitric acid he oxidized tellurium to the dioxide, and from the increase in weight deduced a value for the metal. He published only his final results; from which, if O = 100, Te = 802.121. The three separate experiments give Te = 801.74, 801.786, and 802.838; whence we can calculate the following percentages of metal in the dioxide:

80.057
80.036
80.034

Mean, 80.042, ± .005

The next determinations were made by von Hauer,† who resorted to the analysis of the well crystallized double salt $TeBr_4.2KBr$. In this compound the bromine was estimated as silver bromide, the values assumed for Ag and Br being respectively 108.1 and 80. Recalculating, with our newer atomic weights for the above named elements, we get from v. Hauer's analyses, for 100 parts of the salt, the quantities of AgBr which are put in the third column:

* Poggend. Annal., 28, 395. 1833.
† Sitzungsb. Wien Akad., 25, 142.

2.000 grm. K_2TeBr_6 gave	69.946 per cent. Br.		164.460	
6.668 "	69.8443	"	164.221	
2.934 "	69.9113	"	164.379	
3.697 "	70.0163	"	164.626	
1.000 "	69.901	"	164.355	
			Mean, 164.408,	± .045

From Berzelius' series we may calculate Te = 128.045, and from v. Hauer's Te = 127.419. Dumas,* by a method for which he gives absolutely no particulars, found Te = 129.

In 1879, with direct reference to Mendelejeff's speculations, the subject of the atomic weight of tellurium was taken up by Wills.† The methods of both Berzelius and von Hauer were employed, with various rigid precautions in the way of testing balance and weights, and to ensure purity of material. In the first series of experiments tellurium was oxidized by nitric acid to form TeO_2. The results gave figures ranging from Te = 126.31 to 129.34:

2.21613 grm. Te gave	2.77612 grm. TeO_2.	79.828 per cent. Te.	
1.45313 "	1.81542 "	80.044 "	
2.67093 "	3.33838 "	80.007 "	
4.77828 "	5.95748 "	80.207 "	
2.65029 "	3.31331 "	79.989 "	
		Mean, 80.015,	± .041

In the second series tellurium was oxidized by aqua regia to TeO_2; with results varying from Te = 127.77 to 128.00:

2.85011 grm. Te gave	3.56158 grm. TeO_2.	80.024 per cent. Te.	
3.09673 "	3.86897 "	80.040 "	
5.09365 "	6.36612 "	80.012 "	
3.26604 "	4.08064 "	80.037 "	
		Mean, 80.028,	± .004

Combining these series with that due to Berzelius, we have the following general mean:

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* Ann. d. Chim. et d. Phys., (3,) 55, 129. 1859.

† Journ. Chem. Society, Oct., 1879, p. 704.

Berzelius	80.042, ± .005
Wills, 1st series	80.015, ± .041
" 2d "	80.028, ± .004
General mean	80.035, ± .003

Hence Te = 127.986, ± .035.

By von Hauer's process, the analysis of $TeBr_4.2KBr$, Will's figures give results ranging from Te = 126.07 to 127.61. Reduced to a common standard, 100 parts of the salt yield the quantities of AgBr given in the third column:

1.70673	grm. K_2TeBr_6 gave	2.80499	grm. AgBr.	164.349
1.75225	"	2.88072	"	164.398
2.06938	"	3.40739	"	164.657
3.29794	"	5.43228	"	164.717
2.46545	"	4.05742	"	164.571
			Mean,	164.538, ± .048

Combined with von Hauer's mean, 164.408, ± .045, this gives a general mean of 164.468, ± .033. Hence Te = 127.170, ± .173.

The two independent values for Te combine thus:

From TeO_2	Te =	127.986, ± .035
" TeK_2Br_6	" =	127.170, ± .173
General mean	" =	127.960, ± .034

If O = 16, Te = 128.254.

A careful consideration of the foregoing figures, and of the experimental methods by which they were obtained, will show that they are not absolutely conclusive with regard to the place of tellurium under the periodic law. The atomic weight of iodine, calculated in a previous chapter, is 126.557. Wills' values for Te, rejecting his first series as relatively unimportant, range from 126.07 to 128.00; that is, some of them fall below the atomic weight of iodine, although none descend quite to the 125 assumed by Mendelejeff.

In considering the experimental methods, reference may properly be made to the controversy regarding the atomic weight of antimony. It will be seen that Dexter, estimating the latter constant by the conversion of the metal

into Sb_2O_4, obtained a value approximately of $Sb = 122$. Dumas, working with $SbCl_3$, obtained a similar value. Schneider and Cooke, on the other hand, have established an atomic weight for antimony near 120, and Cooke in particular has traced out the constant errors which lurked unsuspected in the work of Dumas and Dexter. Now in some physical respects tellurium and antimony are quite similar. As constant errors vitiated the recently accepted values for Sb, so they may also effect our estimates for Te. The oxidation of Te by nitric acid resembles in minor particulars that of Sb. The analysis of K_2TeBr_6, gives a low value for Te, and yet the material may have contained traces of oxybromides, the presence of which would render even that lower value too high. A careful revision of the atomic weight of tellurium is still necessary.

VANADIUM.

Roscoe's determination of the atomic weight of vanadium is the only one having any present value. The results obtained by Berzelius * and by Czudnowicz † are unquestionably too high; the error being probably due to the presence of phosphoric acid in the vanadic acid employed. This particular impurity, as Roscoe has shown, prevents the complete reduction of V_2O_5 to V_2O_3 by means of hydrogen. All vanadium ores contain small quantities of phosphorus, which can only be detected with ammonium molybdate; a reaction unknown in Berzelius' time. Furthermore, the complete purification of vanadic acid from all traces of phosphoric acid is a matter of great difficulty, and probably never was accomplished until Roscoe undertook his researches.

In his determination of the atomic weight, Roscoe ‡

* Poggend. Annal., 22, 14. 1831.

† Poggend. Annal., 120, 17. 1863.

‡ Journ. Chem. Soc., 6, pp. 330 and 344. 1868.

studied two compounds of vanadium; namely, the pentoxide, V_2O_5 and the oxychloride, $VOCl_3$. The pentoxide, absolutely pure, was reduced to V_2O_3 by heating in hydrogen, with the following results:

7.7397 grm. V_2O_5 gave 6.3827 grm. V_2O_3.		17.533 per cent. of loss.
6.5819 "	5.4296 "	17.507 "
5.1895 "	4.2819 "	17.489 "
5.0450 "	4.1614 "	17.515 "
5.4296 grm. V_2O_3, reoxidized, gave 6.5814 grm. V_2O_5.		17.501 per cent. difference.
	Mean,	17.509, ± .005

Hence V = 51.264, ± .025.

Upon the oxychloride, $VOCl_3$, two series of experiments were made, one volumetric, the other gravimetric. In the volumetric series the compound was titrated with solutions containing known weights of silver, which had been purified according to the methods recommended by Stas. Roscoe publishes his weighings, and gives percentages deduced from them; his figures, reduced to a common standard, make the quantities of $VOCl_3$ given in the third column proportional to 100 parts of silver. He was assisted by two analysts:

Analyst A.

2.4322 grm. $VOCl_3$	= 4.5525 grm. Ag.	53.425
4.6840 "	8.7505 "	53.528
4.2188 "	7.8807 "	53.533
3.9490 "	7.3799 "	53.510
.9243 "	1.7267 "	53.530
1.4330 "	2.6769 "	53.532

Analyst B.

2.8530 "	5.2853 "	53.980
2.1252 "	3.9535 "	53.755
1.4248 "	2.6642 "	53.479
	Mean,	53.586, ± .039

The gravimetric series, of course, fixes the ratio between $VOCl_3$ and AgCl. If we put the latter at 100 parts, the proportion of $VOCl_3$ comes out as given in the third column:

Analyst A.

1.8521 grm. $VOCl_3$ gave	4.5932 grm. AgCl.		40.323
.7013	"	1.7303	"	40.531
.7486	"	1.8467	"	40.537
1.4408	"	3.5719	"	40.337
.9453	"	2.3399	"	40.399
1.6183	"	4.0282	"	40.174

Analyst B.

2.1936	"	5.4039	"	40.391
2.5054	"	6.2118	"	40.333
			Mean,	40.378, ± .028

These two series give us two values for the molecular weight of $VOCl_3$:

From the volumetric series ... $VOCl_3$ = 173.096, ± .126
" gravimetric " ... " = 173.276, ± .141

General mean .... " = 173.177, ± .094

Hence V = 51.104, ± .104.

Combining the two values for V we get the following result:

From V_2O_5 .... V = 51.264, ± .025
" $VOCl_3$ .... " = 51.104, ± .104

General mean .... " = 51.256, ± .024

Or, if O = 16, V = 51.373.

ARSENIC.

For the determination of the atomic weight of arsenic two compounds have been studied; the chloride and the trioxide. The bromide may also be considered, since it was analyzed by Wallace in order to establish the atomic weight of bromine. His series, in the light of more recent knowledge, may properly be inverted, and applied to the determination of arsenic.

In 1826, Berzelius* heated arsenic trioxide with sulphur

* Poggend. Annal., 8, 1.

in such a way that only SO_2 could escape. 2.203 grammes of As_2O_3, thus treated, gave a loss of 1.069 of SO_2. Hence As = 74.840. This is a close estimation; but, being drawn from a single experiment, has so little weight that it need not be included in our final general mean.

In 1845 Pelouze* applied his method of titration with known quantities of pure silver to the analysis of the trichloride of arsenic, $AsCl_3$. Using the old Berzelian atomic weights, and putting Ag = 1349.01, and Cl = 443.2, he found in three experiments for As the values 937.9, 937.1, and 937.4. Hence 100 parts of silver balance the following quantities of $AsCl_3$:

56.029
56.009
56.016

Mean, 56.018, ± .004

Later, the same method was employed by Dumas,† whose weighings, reduced to the foregoing standard, give the following results:

4.298 grm. $AsCl_3$ =	7.673 grm. Ag.	Ratio, 56.015
5.535 "	9.880 "	56.022
7.660 "	13.686 "	55.970
4.680 "	8.358 "	55.993
		Mean, 56.000, ± .008

The two series of Pelouze and Dumas, combined, give a general mean of 56.014, ± .0035, as the amount of $AsCl_3$ equivalent to 100 parts of silver. Hence As = 74.829, ± .048, a value closely agreeing with that deduced from the single experiment of Berzelius.

The same process of titration with silver was applied by Wallace‡ to the analysis of arsenic tribromide, $AsBr_3$. This compound was repeatedly distilled to ensure purity, and was well crystallized. His weighings show that the quanti-

* Compt. Rend., 20, 1047.

† Ann. Chim. Phys., (3,) 55, 174. 1859.

‡ Philosophical Magazine, (4,) 18, 279.

ties of bromide given in the third column are proportional to 100 parts of silver:

8.3246 grm. $AsBr_3$	= 8.58 grm. Ag.		97.023
4.4368	"	4.573 "	97.022
5.098	"	5.257 "	96.970
		Mean,	97.005, ± .012

Hence As = 74.046, ± .058. Why this value should be so much lower than that from the chloride is unexplained.

The volumetric work done by Kessler,* for the purpose of establishing the atomic weights of chromium and of arsenic, has already been described in the chromium chapter. In that investigation the amount of potassium dichromate required to oxidize 100 parts of As_2O_3 to As_2O_5 was determined, and compared with the quantity of potassium chlorate necessary to produce the same effect. From the molecular weight of $KClO_3$, that of $K_2Cr_2O_7$ was then calculable.

From the same figures, the molecular weights of $KClO_3$ and of $K_2Cr_2O_7$ being both known, that of As_2O_3 may be easily determined. The quantities of the other compounds proportional to 100 parts of As_2O_3 are as follows:

$K_2Cr_2O_7$.	$KClO_3$.
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
	41.199
Mean, 99.045, ± .028	41.224
	41.161
	41.193
	41.149
	41.126
	Mean, 41.172, ± .009

* Poggend. Annal., 95, 204. 1855. Also 113, 134. 1861.

Another series with the bichromate gave the following figures:

	99.08
	99.06
	99.10
	98.97
	98.97
Mean,	99.036, $\pm$ .019
Mean of previous series,	99.045, $\pm$ .028
General mean,	99.039, $\pm$ .016

Other defective series are given to illustrate the partial oxidation of the As_2O_3 by action of air. The foregoing figures give us two distinct values for the molecular weight of As_2O_3. In calculating from the bichromate results the value for chromium deduced from Siewert's determinations will be used, viz., Cr = 52.009, $\pm$ .025.

From $KClO_3$ series	As_2O_3	= 197.996, $\pm$ .049
" $K_2Cr_2O_7$ "	"	= 197.777, $\pm$ .051
General mean	"	= 197.894, $\pm$ .035

Hence As = 75.002, $\pm$ .018.

The general mean for As comes out as follows:

From $AsCl_3$	As	= 74.829, $\pm$ .048
" $AsBr_3$	"	= 74.046, $\pm$ .058
" As_2O_3	"	= 75.002, $\pm$ .018
General mean	"	= 74.918, $\pm$ .016

If O = 16, then As becomes = 75.090.

ANTIMONY.

After some earlier, unsatisfactory determinations, Berzelius,* in 1826, published his final estimation of the atomic weight of antimony. He oxidized the metal by means of nitric acid, and found that 100 parts of antimony gave 124.8 of Sb_2O_4. Hence, if O = 16, Sb = 129.03. The

* Poggend. Annal., 8, 1

value 129 remained in general acceptance until 1855, when Kessler,* by special volumetric methods, showed that it was certainly much too high. Kessler's results will be considered more fully further along, in connection with a later paper; for present purposes a brief statement of his earlier conclusions will suffice. Antimony, and various compounds of antimony, were oxidized partly by potassium anhydrochromate and partly by potassium chlorate; and from the amounts of oxidizing agent required, the atomic weight in question was deduced:

By oxidation of	Sb_2O_3 from 100 parts of Sb ....Sb	= 123.84
"	Sb with $K_2Cr_2O_7$ .... "	= 123.61
"	" $KClO_3 + K_2Cr_2O_7$........ "	= 123.72
"	Sb_2O_3 with " " .... "	= 123.80
"	Sb_2S_3 with $K_2Cr_2O_7$............... "	= 123.58
"	tartar emetic..................... "	= 119.80

The figures given are those calculated by Kessler himself. A recalculation with our newer atomic weights for O, K, Cl, Cr, S, and C, would yield slightly lower values. It will be seen that five of the estimates agree closely, while one diverges widely from the others. It will be shown hereafter that the concordant values are all vitiated by constant errors, and that the exceptional figure is after all the best.

Shortly after the appearance of Kessler's first paper, Schneider† published some results obtained by the reduction of antimony sulphide in hydrogen. The material chosen was a very pure stibnite from Arnsberg, of which the gangue was only quartz. This was corrected for, and corrections were also applied for traces of undecomposed sulphide carried off mechanically by the gas stream, and for traces of sulphur retained by the reduced antimony. The latter sulphur was estimated as barium sulphate. From 3.2 to 10.6 grammes of material were taken in each experiment. The final corrected percentages of S in Sb_2S_3 were as follows:

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* Poggend. Annal., 95, 215.

† Poggend. Annal., 98, 293. 1856. Preliminary note in Bd. 97.

28.559
28.557
28.501
28.554
28.532
28.485
28.492
28.481

Mean, 28.520, $\pm$ .008

Hence, if S = 32, Sb = 120.3.

Immediately after the appearance of Schneider's memoir, Rose * published the result of a single analysis of antimony trichloride, previously made under his supervision by Weber. This analysis, if Cl = 35.5, makes Sb = 120.7, a value of no great weight, but in a measure confirmatory of that obtained by Schneider.

The next research upon the atomic weight of antimony was that of Dexter,† published in 1857. This chemist, having tried to determine the amount of gold precipitable by a known weight of antimony, and having obtained discordant results, finally resorted to the original method of Berzelius. Antimony, purified with extreme care, was oxidized by nitric acid, and the gain in weight was determined. From 1.5 to 3.3 grammes of metal were used in each experiment. The reduction of the weights to a vacuum standard was neglected as being superfluous. From the data obtained, we get the following percentages of Sb in Sb_2O_4:

79.268
79.272
79.255
79.266
79.253
79.271
79.264
79.260
79.286

* Poggend. Annal., 98, 455. 1856.
† Poggend. Annal., 100, 563.

79.274
79.232
79.395
79.379
Mean, 79.283, ± .009

Hence, if O = 16, Sb = 122.46.

The determinations of Dumas* were published in 1859. This chemist sought to fix the ratio between silver and antimonious chloride, and obtained results for the atomic weight of antimony quite near to those of Dexter. The $SbCl_3$ was prepared by the action of dry chlorine upon pure antimony; it was distilled several times over antimony powder, and it seemed to be perfectly pure. Known weights of this preparation were added to solutions of tartaric acid in water, and the silver chloride was precipitated without previous removal of the antimony. Here, as Cooke has since shown, is a possible source of error, for under such circumstances the crystalline argento-antimonious tartrate may also be thrown down and contaminate the chloride of silver. But be that as it may; Dumas' weighings, reduced to a common standard, give as proportional to 100 parts of silver, the quantities of $SbCl_3$ which are stated in the third of the subjoined columns:

1.876 grm. $SbCl_3$	= 2.660 grm. Ag.	70.526
4.336 "	6.148 "	70.527
5.065 "	7.175 "	70.592
3.475 "	4.930 "	70.487
3.767 "	5.350 "	70.411
5.910 "	8.393 "	70.416
4.828 "	6.836 "	70.626
	Mean,	70.512, ± .021

Hence, if Ag = 108, and Cl = 355, Sb = 122.

In 1861 Kessler's second paper† relative to the atomic weight of antimony appeared. Kessler's methods were somewhat complicated, and for full details the original memoirs must be consulted. A standard solution of potassium anhydrochromate was prepared, containing 6.1466

* Ann. Chim. Phys., (3,) 55, 175.

† Poggend. Annal., 113, 145.

grammes to the litre. With this, solutions containing known quantities of antimony or of antimony compounds were titrated, the end reaction being adjusted with a standard solution of ferrous chloride. In some cases the titration was preceded by the addition of a definite weight of potassium chlorate, insufficient for complete oxidation; the anhydrochromate then served to finish the reaction. The object in view was to determine the amount of oxidizing agent, and therefore of oxygen, necessary for the conversion of known quantities of antimonious into antimonic compounds.

In the later paper Kessler refers to his earlier work, and shows that the values then found for antimony were all too high, except in the case of the series made with tartar emetic. That series he merely states, and subsequently ignores, evidently believing it to be unworthy of further consideration. For the remaining series he points out the sources of error. These need not be rediscussed here, as the discussion would have no value for present purposes; suffice it to say that in the series representing the oxidation of Sb_2O_3 with anhydrochromate and chlorate, the material used was found to be impure. Upon estimating the impurity and correcting for it, the earlier value of Sb = 123.80 becomes Sb = 122.36, according to Kessler's calculations.

In the paper now under consideration four series of results are given. The first represents experiments made upon a pure antimony trioxide which had been sublimed, and which consisted of shining colorless needles. This was dissolved, together with some potassium chlorate, in hydrochloric acid, and titrated with anhydrochromate solution. Six experiments were made, but Kessler rejects the first and second as untrustworthy. The data for the others are as follows:

Sb_2O_3.	$KClO_3$.	$K_2Cr_2O_7$ *sol. in cc.*
1.7888 grm.	.4527 grm.	19.2 cc.
1.6523 "	.4506 "	3.9 "
3.2998 "	.8806 "	16.5 "
1.3438 "	.3492 "	10.2 "

From these figures Kessler deduces Sb = 122.16.

These data, reduced to a common standard, give the following quantities of oxygen needed to oxidize 100 parts of Sb_2O_3 to Sb_2O_5. Each cubic centimetre of the $K_2Cr_2O_7$ solution corresponds to one milligramme of O:

10.985
10.939
10.951
10.936

Mean, 10.953, ± .0075

In the second series of experiments pure antimony was dissolved in hydrochloric acid with the aid of an unweighed quantity of potassium chlorate. The solution, containing both antimonious and antimonic compounds, was then reduced entirely to the antimonious condition by means of stannous chloride. The excess of the latter was corrected with a strong hydrochloric acid solution of mercuric chloride, then, after diluting and filtering, a weighed quantity of potassium chlorate was added, and the titration with anhydrochromate was performed as usual. Calculated as above, the percentages of oxygen given in the last column correspond to 100 parts of antimony:

Sb.	*$KClO_3$.*	*$K_2Cr_2O_7$ sol. cc.*	*Per cent. O.*
1.636 grm.	0.5000 grm.	18.3	13.088
3.0825 "	0.9500 "	30.2	13.050
4.5652 "	1.4106 "	45.5	13.098

Mean, 13.079, ± .0096

This series gave Kessler Sb = 122.34.

The third and fourth series of experiments were made with pure antimony trichloride, $SbCl_3$, prepared by the action of mercuric chloride upon metallic antimony. This preparation, in the third series, was dissolved in hydrochloric acid, and titrated. In one experiment solid $K_2Cr_2O_7$ in weighed amount was added before titration: in the other two estimations $KClO_3$ was taken as usual. If, according to Siewert's work, we take Cr = 52.009, the percentages of oxygen in the last column correspond to 100 parts of $SbCl_3$:

						Per cent. O.
1.8576 grm. $SbCl_3$ needed	.5967 grm.	$K_2Cr_2O_7$	and	33.4	cc. sol.	7.0338
1.9118 "	.3019 "	$KClO_3$	"	16.2	"	7.0321
4.1235 "	.6801 "	"	"	23.2	"	7.0222
					Mean,	7.0294, ± .0024

The fourth set of experiments was gravimetric. The solution of $SbCl_3$, mixed with tartaric acid, was first precipitated by hydrogen sulphide, in order to remove the antimony. The excess of H_2S was corrected by copper sulphate, and then the chlorine was estimated as silver chloride in the ordinary manner. 100 parts of AgCl correspond to the amounts of $SbCl_3$ given in the third column.

1.8662 grm. $SbCl_3$ gave	3.483 grm. AgCl.		53.580
1.6832 "	3.141 "		53.588
2.7437 "	5.1115 "		53.677
2.6798 "	5.0025 "		53.569
5.047 "	9.411 "		53.629
3.8975 "	7.2585 "		53.696
		Mean,	53.623, ± .015

The volumetric series with $SbCl_3$ gave Kessler values for Sb ranging from 121.16 to 121.47. The gravimetric series, on the other hand, yielded results from Sb = 124.12 to 124.67. This discrepancy Kessler rightly attributes to the presence of oxygen in the chloride; and, ingeniously correcting for this error, he deduces from both sets combined, the value of Sb = 122.37.

The several mean results for antimony agree so fairly with each other, and with the estimates obtained by Dexter and Dumas, that we cannot wonder that Kessler felt satisfied of their general correctness, and of the inaccuracy of the figures published by Schneider. Still, the old series of data obtained by the titration of tartar emetic with anhydrochromate contained no evident errors, and was not accounted for. This series,* if we reduce all of Kessler's figures to a single common standard, give a ratio between $K_2Cr_2O_7$ and $C_4H_4KSbO_7.\frac{1}{2}H_2O$. 100 parts of the former will oxidize of the latter:

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* Poggend. Annal., 95, 217.

336.64
338.01
336.83
337.93
338.59
335.79
Mean, 337.30, ± .29

From this, if $K_2Cr_2O_7 = 294.64$, $Sb = 119.8$.

The newer atomic weights found in the previous chapters of this work will be applied to the discussion of all these series further along. It may, however, be properly noted at this point, that the probable errors assigned to the percentages of oxygen in three of Kessler's series are too low. These percentages are calculated from the quantities of $KClO_3$ involved in the several reactions, and their probable errors should be increased with reference to the probable error of the molecular weight of that salt. The necessary calculations would be more laborious than the importance of the figures would warrant, and, accordingly, in computing the final general mean for antimony, Kessler's figures will receive somewhat higher weight than they are legitimately entitled to.

Naturally, the concordant results of Dexter, Kessler, and Dumas led to the general acceptance of the value of 122 for antimony as against the lower figure 120 of Schneider. Still, in 1871, Unger* published the results of a single analysis of Schlippe's salt, $Na_3SbS_4.9H_2O$. This analysis gave $Sb = 119.76$, if $S = 32$ and $Na = 23$, but no great weight could be attached to the determination. It served, nevertheless, to show that the controversy over the atomic weight of antimony was not finally settled.

More than ten years after the appearance of Kessler's second paper the subject of the atomic weight of antimony was again taken up, this time by Professor Cooke. His results appeared in the autumn of 1877,† and were conclusive in favor of the lower value, approximately 120. For full

* Archiv. der Pharmacie, 197, 194. Quoted by Cooke.

† Proceedings American Academy, v. 13.

details the original memoir must be consulted; only a few of the leading points can be cited here.

Schneider analyzed a sulphide of antimony which was already formed. Cooke, reversing the method, effected the synthesis of this compound. Known weights of pure antimony were dissolved in hydrochloric acid containing a little nitric acid. In this solution weighed balls of antimony were boiled until the liquid became colorless; subsequently the weight of metal lost by the balls was ascertained. To the solution, which now contained only antimonious compounds, tartaric acid was added, and then, with a supersaturated aqueous sulphhydric acid, antimony trisulphide was precipitated. The precipitate was collected by an ingenious process of reverse filtration, converted into the black modification by drying at 210°, and weighed. After weighing, the Sb_2S_3 was dissolved in hydrochloric acid, leaving a carbonaceous residue unacted upon. This was carefully estimated and corrected for. About two grammes of antimony were taken in each experiment and thirteen syntheses were performed. In two of these, however, the antimony trisulphide was weighed only in the red modification, and the results were uncorrected by conversion into the black variety and estimation of the carbonaceous residue. In fact, every such conversion and correction was preceded by a weighing of the red modification of the Sb_2S_3. The mean result of these weighings, if S = 32, gave Sb = 119.994. The mean result of the corrected syntheses gave Sb = 120.295. In these eleven experiments the following percentages of S in Sb_2S_3 were established:

28.57
28.60
28.57
28.43
28.42
28.53
28.50
28.49
28.58
28.50
28.51

Mean, 28.5182, ± .0120

These results, confirmatory of the work of Schneider, were presented to the American Academy in 1876. Still, before publication, Cooke thought it best to repeat the work of Dumas, in order to detect the cause of the old discrepancy between the values Sb = 120 and Sb = 122. Accordingly, various samples of antimony trichloride were taken, and purified by repeated distillations. The final distillate was further subjected to several recrystallizations from the fused state; or, in one case, from a saturated solution in bisulphide of carbon. The portions analyzed were dissolved in concentrated aqueous tartaric acid, and precipitated by silver nitrate, many precautions being observed. The silver chloride was collected by reverse filtration, and dried at temperatures from 110° to 120°. In one experiment the antimony was first removed by H_2S. Seventeen experiments were made, giving, if Ag = 108 and Cl = 35.5, a mean value of Sb = 121.94. If we reduce to a common standard, Cooke's analyses give, as proportional to 100 parts of AgCl, the quantities of $SbCl_3$ stated in the third column:

1.5974 grm. $SbCl_3$	gave	3.0124 grm. AgCl.		53.028
1.2533	"	2.3620	"	53.061
.8876	"	1.6754	"	52.978
.8336	"	1.5674	"	53.184
.5326	"	1.0021	"	53.148
.7270	"	1.3691	"	53.101
1.2679	"	2.3883	"	53.088
1.9422	"	3.6646	"	52.999
1.7702	"	3.3384	"	53.025
2.5030	"	4.7184	"	53.048
2.1450	"	4.0410	"	53.081
1.7697	"	3.3281	"	53.175
2.3435	"	4.4157	"	53.072
1.3686	"	2.5813	"	53.020
1.8638	"	3.5146	"	53.030
2.0300	"	3.8282	"	53.028
2.4450	"	4.6086	"	53.053

Mean, 53.066, ± .0096

This mean may be combined with that of Kessler's series, as follows:

Kessler	53.623, ± .015
Cooke	53.066, ± .0096
General mean	53.2311, ± .008

The results thus obtained with $SbCl_3$ confirmed Dumas' determination of the atomic weight of antimony as remarkably as the syntheses of Sb_2S_3 had sustained the work of Schneider. Evidently, in one or the other series a constant error must be hidden, and much time was spent by Cooke in searching for it. It was eventually found that the chloride of antimony invariably contained traces of oxychloride, an impurity which tended to increase the apparent atomic weight of the metal under consideration. It was also found, in the course of the investigation, that hydrochloric acid solutions of antimonious compounds oxidize in the air during boiling as rapidly as ferrous compounds; a fact which explains the high values for antimony found by Kessler.

In order to render "assurance doubly sure," Professor Cooke also undertook the analysis of the bromide and the iodide of antimony. The bromide, $SbBr_3$, was prepared by adding the finely powdered metal to a solution of bromine in carbon disulphide. It was purified by repeated distillation over pulverized antimony, and by several recrystallizations from bisulphide of carbon. The bromine determinations resembled those of chlorine, and gave, if Ag = 108 and Br = 80, a mean value for antimony of Sb = 120. Reduced to a common standard, the fifteen analyses give the subjoined quantities of $SbBr_3$ proportional to 100 parts of silver bromide:

1.8621	grm. $SbBr_3$ gave	2.9216	grm. AgBr.	63.736
.9856	"	1.5422	"	63.909
1.8650	"	2.9268	"	63.721
1.5330	"	2.4030	"	63.795
1.3689	"	2.1445	"	63.833
1.2124	"	1.8991	"	63.841
.9417	"	1.4749	"	63.848
2.5404	"	3.9755	"	63.901
1.5269	"	2.3905	"	63.874
1.8604	"	2.9180	"	63.756
1.7298	"	2.7083	"	63.870

3.2838 grm. $SbBr_3$ gave	5.1398 grm. AgBr.		63.890
2.3589	"	3.6959	"	63.825
1.3323	"	2.0863	"	63.859
2.6974	"	4.2285	"	63.791

Mean, 63.830, ± .008

The iodide of antimony was prepared like the bromide, and analyzed in the same way. At first, discordant results were obtained, due to the presence of oxyiodide in the iodide studied. The impurity, however, was removed by subliming the iodide in an atmosphere of dry carbon dioxide. With this purer material, seven estimations of iodine were made, giving, if Ag = 108 and I = 127, a value for antimony of Sb = 120. Reduced to a uniform standard, Cooke's weighings give the following quantities of SbI_3 proportional to 100 parts of silver iodide:

1.1877 grm. SbI_3 gave		1.6727 grm. AgI.		71.005
.4610	"	.6497	"	70.956
3.2527	"	4.5716	"	71.150
1.8068	"	2.5389	"	71.165
1.5970	"	2.2456	"	71.117
2.3201	"	3.2645	"	71.071
.3496	"	.4927	"	70.956

Mean, 71.060, ± .023

Although Cooke's work was practically conclusive, as between the rival values for antimony, his results were severely criticized by Kessler,* who, evidently, had read Cooke's paper in a very careless way. On the other hand, Schneider published in Poggendorff's Annalen a friendly review of the new determinations, which so splendidly vindicated his own accuracy. In reply to Kessler, Cooke undertook still another series of experiments with antimony bromide,† and obtained absolute confirmation of his previous results. To a solution of antimony bromide was added a solution containing a known weight of silver not quite sufficient to precipitate all the bromine. The excess

* Berichte d. Deutsch. Chem. Gesell., 12, 1044. 1879.

† Amer. Journ. Sci. and Arts, May, 1880. Berichte, 13, 951.

of the latter was estimated by titration with a normal silver solution. Five analyses gave values for antimony ranging from 119.98 to 120.02, when Ag = 108 and Br = 80. Reduced to a common standard, the weights obtained gave the amounts of $SbBr_3$ stated in the third column as proportional to 100 parts of silver:

2.5032 grm. $SbBr_3$	= 2.2528 grm. Ag.	111.115
2.0567 "	1.8509 "	111.119
2.6512 "	2.3860 "	111.115
3.3053 "	2.9749 "	111.106
2.7495 "	2.4745 "	111.113
		Mean, 111.114, ± .0014

Schneider,* also, in order to more fully answer Kessler's objections, repeated his work upon the Arnsberg stibnite. This he reduced in hydrogen as before, correcting scrupulously for impurities. The following percentages of sulphur were found:

28.546
28.534
28.542

Mean, 28.541, ± .0024

These figures confirm his old results, and may be fairly combined with them and with the percentages found by Cooke, as follows:

Schneider, early series	28.520, ± .008
" late "	28.541, ± .0024
Cooke	28.5182, ± .0120
General mean	28.5385, ± .0023

We have now before us the following ratios, good and bad, from which to calculate the atomic weight of antimony. The single results obtained by Weber and by Unger, being unimportant, are not included:

(1.) Percentage of S in Sb_2S_3, 28.5385, ± .0023
(2.) " Sb in Sb_2O_4, 79.283, ± .009
(3.) O needed to oxidize 100 parts $SbCl_3$, 7.0294, ± .0024
(4.) O " " Sb_2O_3, 10.953, ± .0075
(5.) O " " Sb, 13.079, ± .0096

* Journ. für Prakt. Chem., (2,) 22, 131.

(6.) $K_2Cr_2O_7$: tartar emetic : : 100 : 337.30, ± .29
(7.) Ag : $SbCl_3$: : 100 : 70.512, ± .021
(8.) AgCl : $SbCl_3$: : 100 : 53.2311, ± .008
(9.) Ag : $SbBr_3$: : 100 : 111.114, ± .0014
(10.) AgBr : $SbBr_3$: : 100 : 63.830, ± .008
(11.) AgI : SbI_3 : : 100 : 71.060, ± .023

Three of these ratios give estimates for the molecular weight of antimony trichloride, and two give corresponding values for the bromide. These values may be combined, as follows: First, for the chloride we have—

From (3)	$SbCl_3$	= 227.094, ± .115
" (7)	"	= 227.771, ± .091
" (8)	"	= 228.433, ± .039
General mean	"	= 228.225, ± .034

Hence Sb = 122.115, ± .055.

For the bromide we get:

From (9)	$SbBr_3$	= 358.926, ± .032
" (10)	"	= 358.935, ± .060
General mean	"	= 358.929, ± .029

Hence Sb = 119.625, ± .063.

From all the data eight values for Sb may be deduced. These fall into two groups; the one near the number 120, the other not far from 122. In making the calculation the atomic weights found in previous chapters are applied; the value selected for chromium being that deduced from Siewert's experiments:

1.	From Sb_2S_3, ratio (1)	Sb	= 120.145, ± .045	Low.
2.	" $SbBr_3$	"	= 119.625, ± .063	
3.	" SbI_3, ratio (11)	"	= 119.665, ± .179	
4.	" tartar emetic, ratio (6)	"	= 118.690, ± .278	
5.	" Sb_2O_4, ratio (2)	"	= 122.181, ± .061	High.
6.	" $SbCl_3$	"	= 122.115, ± .055	
7.	" ratio (4)	"	= 121.798, ± .105	
8.	" " (5)	"	= 122.053, ± .094	
	General mean	"	= 121.027, ± .025	
	General mean of values 1 to 4	"	= 119.935, ± .036	
	" " 5 " 8	"	= 122.092, ± .035	

Although the means of the four lower values and of the four higher values are thus shown to be approximately

equal in weight, we know from Cooke's experiments that the larger mean is vitiated by serious constant errors. Only in value 5, the result calculated from Dexter's experiments, has the constant error not been pointed out. Cooke considers it probable, however, that the Sb_2O_4 involved in this work contained traces of some lower oxide, which, if present, would render the atomic weight of antimony apparently too high. Chemically considered, the preponderance of evidence is strongly in favor of values 1 to 3, deduced from the experiments of Schneider and of Cooke. These give a general mean of Sb = 119.955, ± .036; or, if O = 16, this becomes Sb = 120.231.

This we may accept as most nearly the true result, and reject the data of Dexter, Dumas, and Kessler altogether.

Since this chapter was written, Pfeifer has compared the amount of antimony thrown down electrolytically, with the quantity of silver deposited by the same current in the same time. From rather meagre data he concludes that the atomic weight of antimony, thus determined, may be 121. Additional investigation is promised. The figures thus far published would weigh little as against Cooke's experiments. (Ann. Chem. Pharm., 209, 161. 1881.)

BISMUTH.

Early in the century the combining weight of bismuth was approximately fixed through the experiments of Lagerhjelm.* Effecting the direct union of bismuth and sulphur, he found that ten parts of the metal yield the following quantities of trisulphide:

	12.2520
	12.2065
	12.2230
	12.2465
Mean,	12.2320

* Annals of Philosophy, 4, 358. 1814. Results adopted by Berzelius.

Hence B = 215 in round numbers, a value now known to be much too high. Lagerhjelm also oxidized bismuth with nitric acid, and, after ignition, weighed the trioxide thus formed. Ten parts of metal gave the following quantities of Bi_2O_3:

11.1382
11.1275

Mean, 11.13285

Hence, if O = 16, Bi = 211.85, a figure still too high.

In 1851 the subject of the atomic weight of bismuth was taken up by Schneider,* who, like Lagerhjelm, studied the oxidation of the metal with nitric acid. The work was executed with a variety of experimental refinements, by means of which every error due to possible loss of material was carefully avoided. For full details the original paper must be consulted; there is only room in these pages for the actual results, as follows. The figures represent the percentages of Bi in Bi_2O_3:

89.652
89.682
89.644
89.634
89.656
89.666
89.655
89.653

Mean, 89.6552, $\pm$ .0034

Hence Bi = 207.523, $\pm$ .082; or, if O = 16, Bi = 208.001.

Finally, we come to the results obtained by Dumas.† Bismuth trichloride was prepared by the action of dry chlorine upon bismuth, and repeatedly rectified by distillation over bismuth powder. The product was weighed in a closed tube, dissolved in water, and precipitated with sodium carbonate. In the filtrate, after strongly acidulating

* Poggend. Annal., 82, 303. 1851.
† Ann. de Chim. et de Phys., (3,) 55, 176. 1859.

with nitric acid, the chlorine was precipitated by a known amount of silver. The figures in the third column show the quantities of $BiCl_3$ proportional to 100 parts of silver:

3.506 grm. $BiCl_3$ =	3.545 grm. Ag.	98.900
1.149 "	1.168 "	98.373
1.5965 "	1.629 "	98.005
2.1767 "	2.225 "	97.829
3.081 "	3.144 "	97.996
2.4158 "	2.470 "	97.806
1.7107 "	1.752 "	97.643
3.523 "	3.6055 "	97.712
5.241 "	5.361 "	97.762
		Mean, 98.003, ± .090

Hence Bi = 210.464, ± .294.

The first three of the foregoing series of experiments were made with slightly discolored material, and may therefore be rejected. The remaining six percentages give a mean of 97.791; whence Bi = 209.78; or, if O = 16, Bi = 210.26.

As between the unaccordant results of Schneider and of Dumas, those of the former chemist are probably nearest correct. His method of determination was the more reliable, and the details which he gives concerning his manipulations afford strong presumptions of accuracy. Doubtless the bismuth trichloride used by Dumas, contained, like the corresponding antimony compounds, traces of oxychloride. We may fairly assume, for all practical purposes, that the atomic weight of bismuth cannot be far from 208.

TIN.

Stannic oxide and stannic chloride are the compounds which have been studied in estimating the atomic weight of tin.

The composition of stannic oxide has been fixed in two ways; by synthesis from the metal, and by reduction in hydrogen. For the first method we may consider the work of Berzelius, Mulder and Vlaanderen, and Dumas.

Berzelius* oxidized 100 parts of tin by nitric acid, and found that 127.2 parts of SnO_2 were formed.

The work done by Mulder and Vlaanderen† was done in connection with a long investigation into the composition of Banca tin, which was found to be almost absolutely pure. For the atomic weight determinations, however, really pure tin was taken, prepared from pure tin oxide. This metal was oxidized by nitric acid, with the following results. 100 parts of tin gave of SnO_2:

127.56—Mulder.
127.56—Vlaanderen.
127.43— "

Mean, 127.517, ± .029

Dumas‡ oxidized pure tin by nitric acid in a flask of glass. The resulting SnO_2 was strongly ignited, first in the flask, and afterwards in platinum. His weighings, reduced to the foregoing standard, give for dioxide from 100 parts of tin the amounts stated in the third column:

12.443 grm. Sn gave	15.820 grm. SnO_2.	127.14
15.976 "	20.301 "	127.07
	Mean,	127.105, ± .024

In an investigation later than that previously cited, Vlaanderen|| found that when tin was oxidized in glass or porcelain vessels, and the resulting oxide ignited in them, traces of nitric acid were retained. When, on the other hand, the oxide was strongly heated in platinum, the latter was perceptibly attacked, so much so as to render the results uncertain. He therefore, in order to fix the atomic weight of tin, reduced the oxide by heating it in a porcelain boat in a stream of hydrogen. Two experiments gave Sn = 118.08, and Sn = 118.24. These, when O = 16, become, if reduced to the above common standard,

* Poggend. Annal., 8, 177.
† Journ. für Prakt. Chem., 49, 35. 1849.
‡ Ann. Chem. Pharm., 113, 26.
|| Jahresbericht, 1858, 183.

127.100
127.064

Mean, 127.082, ± .012

We have now four series of results showing the quantity of SnO_2 formed from 100 parts of tin. To Berzelius' single value may be assigned the probable error of a single experiment in Mulder and Vlaanderen's series:

Berzelius	127.200, ± .041	—Oxidation.
Mulder and Vlaanderen	127.517, ± .029	— "
Dumas	127.105, ± .024	— "
Vlaanderen	127.082, ± .012	—Reduction.
General mean	127.143, ± .0098	

Dumas, in the paper previously quoted, also gives the results of some experiments with stannic chloride, $SnCl_4$. This was titrated with a solution containing a known weight of silver. From the weighings given, 100 parts of silver correspond to the quantities of $SnCl_4$ named in the third column:

1.839 grm. $SnCl_4$ =	3.054 grm. Ag.	60.216
2.665 "	4.427 "	60.199

Mean, 60.207, ± .006

All these data properly combined give us the following values for the atomic weight of tin:

From SnO_2 Sn = 117.624, ± .050
" $SnCl_4$ " = 117.832, ± .067

General mean " = 117.698, ± .040

If O = 16, this becomes Sn = 117.968.

TITANIUM.

The earliest determinations of the atomic weight of titanium are due to Heinrich Rose.* In his first investigation he studied the conversion of titanium sulphide into titanic acid, and obtained erroneous results; later, in 1829, he published his analyses of the chloride.† This compound was purified by repeated rectifications over mercury and over potassium, and was weighed in bulbs of thin glass. These were broken under water in tightly stoppered flasks; the titanic acid was precipitated by ammonia, and the chlorine was estimated as silver chloride. The following results were obtained. In a fourth column I give the TiO_2 in percentages referred to $TiCl_4$ as 100; and in a fifth column the quantity of $TiCl_4$ proportional to 100 parts of AgCl:

$TiCl_4$.	TiO_2.	AgCl.	Per cent. TiO_2.	AgCl Ratio.
.885 grm.	.379 grm.	2.661 grm.	42.825	33.258
2.6365 "	1.120 "	7.954 "	42.481	33.147
1.7157 "	.732 "	5.172 "	42.665	33.173
3.0455 "	1.322 "	9.198 "	43.423	33.100
2.4403 "	1.056 "	7.372 "	43.273	33.102
			Mean, 42.933, ± .121	33.156, ± .019

If we directly compare the AgCl with the TiO_2 we shall find 100 parts of the former proportional to the following quantities of the latter:

14.243
14.081
14.153
14.373
14.324

Mean, 14.235, ± .036

From all these figures we can get three values for Ti, thus:

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* Gilbert's Annalen, 1823, 67 and 129.

† Poggend. Annal., 15, 145. Berz. Lehrbuch, 3, 1210.

From per cent. TiO_2	Ti	= 50.493,	± .410
" AgCl : $TiCl_4$	"	= 48.232,	± .127
" AgCl : TiO_2	"	= 49.523,	± .206
General mean	"	= 48.710,	± .105

These results will be discussed further along in connection with others.

Shortly after the appearance of Rose's paper, Mosander* published some figures giving the percentages of oxygen in titanium dioxide, from which a value for the atomic weight of titanium was deduced. Although no details are furnished as to experimental methods, and no actual weighings are given, I cite his percentages for whatever they may be worth:

40.814
40.825
40.610
40.180
40.107
40.050
40.780
40.660
39.830

Mean, 40.428

These figures give values for Ti ranging from 46.277 to 48.231; or, in mean, Ti = 47.045. They are not, however, sufficiently explicit to deserve any further consideration. It will be noticed that the highest value nearly coincides with Rose's lowest.

In 1847 Isidor Pierre made public a series of important determinations.† Titanium chloride, free from silicon and from iron, was prepared by the action of chlorine upon a mixture of carbon with pure, artificial, titanic acid. This chloride was weighed in sealed tubes, these were broken under water, and the resulting hydrochloric acid was titrated with a standard solution of silver after the method

* Berz. Jahresbericht, 10, 108. 1831.
† Ann. de Chim. et Phys., (3,) 20, 257.

of Pelouze. I subjoin Pierre's weighings, and add, in a third column, the ratio of $TiCl_4$ to 100 parts of silver:

$TiCl_4$.	*Ag.*	*Ratio.*
.8215 grm.	1.84523 grm.	44.520
.7740 "	1.73909 "	44.506
.7775 "	1.74613 "	44.527
.7160 "	1.61219 "	44.412
.8085 "	1.82344 "	44.339
.6325 "	1.42230 "	44.470
.8155 "	1.83705 "	44.392
.8165 "	1.83899 "	44.399
.8065 "	1.81965 "	44.322

Mean, 44.432, ± .0173

It will be seen that the first three of these results agree well with each other and are much higher than the remaining six. The last four experiments were made purposely with tubes which had been previously opened, in order to determine the cause of the discrepancy. According to Pierre, the opening of a tube of titanium chloride admits a trace of atmospheric moisture. This causes a deposit of titanic acid near the mouth of the tube, and liberates hydrochloric acid. The latter gas being heavy, a part of it falls back into the tube, so that the remaining chloride is richer in chlorine and poorer in titanium than it should be. Hence, upon titration, too low figures for the atomic weight of titanium are obtained. Pierre accordingly rejects all but the first three of the above estimations:

From all of Pierre's.........Ti = 49.889, ± .096
" the first three......... " = 50.259, ± .063

The memoir of Pierre upon the atomic weight of titanium was soon followed by a paper from Demoly,* who obtained much higher results. He also started out from titanic chloride, which was prepared from rutile. The latter substance was found to contain 1.8 per cent. of silica; whence Demoly inferred that the $TiCl_4$ investigated by Rose and by Pierre

* Ann. Chem. Pharm., 72, 214. 1849. Berz. Jahresb., 30, 58.

might have been contaminated with $SiCl_4$, an impurity which would lower the value deduced for the atomic weight under consideration. Accordingly, in order to eliminate all such possible impurities, this process was resorted to: the chloride, after rectification over mercury and potassium, was acted upon by dry ammonia, whereupon the compound $TiCl_4.4NH_3$ was deposited as a white powder. This was ignited in dry ammonia gas, and the residue, by means of chlorine, was reconverted into titanic chloride, which was again repeatedly rectified over mercury, potassium, and potassium amalgam. The product boiled steadily at 135°. This chloride, after weighing in a glass bulb, was decomposed by water, the titanic acid was precipitated by ammonia, and the chlorine was estimated in the filtrate as silver chloride. Three analyses were performed, yielding the following results. I give the actual weighings:

1.470 grm. $TiCl_4$ gave	4.241 grm. AgCl and	.565 grm. TiO_2.
2.330 "	6.752 "	.801 "
2.880 "	8.330 "	1.088 "

The ".801" in the last column is certainly a misprint for .901. Assuming this correction, the results may be given in three ratios, thus:

Per cent. TiO_2 from $TiCl_4$.	*$TiCl_4$: 100 AgCl.*	*TiO_2 : 100 AgCl.*
38.435	34.662	13.322
38.669	34.508	13.344
37.778	34.574	13.061
Mean, 38.294, ± .180	34.581, ± .030	13.242, ± .061

These three ratios give three widely divergent values for the atomic weight of titanium:

From per cent. TiO_2 .... Ti = 36.063, ± .519
" AgCl : TiO_2 .... " = 43.841, ± .350
" AgCl : $TiCl_4$ .... " = 56.386, ± .181

General mean .... " = 52.191, ± .153

The value assumed by Demoly is 56; who employs but one ratio and ignores practically the others.

Upon comparing Demoly's figures with those obtained by Rose, certain points of similarity are plainly to be noted. Both sets of results were reached by essentially the same method; and in both the discordance between the percentages of titanic acid and of silver chloride is glaring. This discordance can rationally be accounted for by assuming that the titanic chloride was in neither case absolutely what it purported to be: that, in brief, it must have contained impurities; such for example as hydrochloric acid, as shown in the experiments of Pierre, or possibly traces of oxychlorides. Considerations of this kind also throw doubt upon the results attained by Pierre, for he neglected the direct estimation of the titanic acid altogether, thus leaving us without means for correctly judging as to the character of his material. In fact, not one of the determinations of the atomic weight of titanium can be regarded as trustworthy. All depend upon the chloride, and the volatile chlorides of metals are as a class especially liable to contaminations of a kind most difficult to recognize. Possibly a series of good determinations might be based upon analyses of some of the titanofluorides. I subjoin a combination of the foregoing mean values, feeling that such a general average is a little better than any one set of determinations taken singly:

From Rose's analyses	Ti	= 48.710, ± .105
" Pierre's "	"	= 49.889, ± .096
" Demoly's "	"	= 52.191, ± .153
General mean	"	= 49.846, ± .064

Or, if O = 16, Ti = 49.961.

This mean agrees with the average of all of Pierre's experiments.

ZIRCONIUM.

The atomic weight of zirconium has been determined by Berzelius, by Hermann, and by Marignac. Berzelius* ignited the neutral sulphate, and thus ascertained the ratio in it between the ZrO_2 and the SO_3. Putting SO_3 at 100, he gives the following proportional quantities of ZrO_2:

75.84
75.92
75.80
75.74
75.97
75.85

Mean, 75.853, ± .023

Hence Zr = 89.255, ± .039; or, if O = 16, then Zr = 89.461.

Hermann's† estimate of the atomic weight of zirconium was based upon analyses of the chloride, concerning which he gives no details or weighings. From sublimed zirconium chloride he finds Zr = 831.8, when O = 100; and from two lots of the basic chloride $2ZrOCl_2.9H_2O$, Zr = 835.65 and 851.40 respectively. The mean of all three is 839.62; whence, with modern formulæ and O = 15.9633, Zr becomes = 89.354.

Marignac's results‡ were obtained by analyzing the double fluoride of zirconium and potassium. His weights are as follows:

1.000 grm.	gave	.431	grm. ZrO_2 and	.613	grm. K_2SO_4.
2.000	"	.864	"	1.232	"
.654	"	.282	"	.399	"
5.000	"	2.169	"	3.078	"

These figures give us three ratios. A, the ZrO_2 from 100

* Poggend. Annal., 4, 126. 1825.
† Journ. für Prakt. Chem., 31, 77. Berz. Jahresb., 25, 147.
‡ Ann. Chim. Phys., (3,) 60, 270. 1860.

parts of salt; B, the K_2SO_4 from 100 parts of salt; and C, the ZrO_2 proportional to 100 parts of K_2SO_4:

	A.	B.	C.
	43.100	61.300	70.310
	43.200	61.600	70.130
	43.119	61.000	70.677
	43.380	61.560	70.468
Mean,	43.200, $\pm$ .043	61.365, $\pm$ .094	70.396, $\pm$ .079

From A	Zr = 89.775, $\pm$ .216
" B	" = 91.408, $\pm$ .437
" C	" = 90.476, $\pm$ .138
General mean	" = 90.328, $\pm$ .113

Or, if O = 16, Zr = 90.536.

Combining with Berzelius' work we get this result:

Berzelius	Zr = 89.255, $\pm$ .039
Marignac	" = 90.328, $\pm$ .113
General mean	" = 89.367, $\pm$ .037

Or, if O = 16, Zr = 89.573.

These figures need little criticism. They show conclusively that the atomic weight of zirconium ought to be redetermined. Probably the method employed by Berzelius was the best with respect to manipulation, while on the other hand it is likely that Marignac worked with purer material. Hermann's experiments could hardly have yielded certain results, since the zirconium chloride might so easily become contaminated with traces of moisture and thence of oxygen.

THORIUM.

The atomic weight of thorium has been determined from analyses of the sulphate, oxalate, formate, and acetate, with widely varying results. The earliest figures are due to Berzelius,* who worked with the sulphate, and with the double sulphate of potassium and thorium. The thoria was precipitated by ammonia, and the sulphuric acid was estimated as $BaSO_4$. The sulphate gave the following ratios in two experiments. The third column represents the weight of ThO_2 proportional to 100 parts of $BaSO_4$:

.6754 grm. ThO_2 =	1.159 grm. $BaSO_4$.	Ratio, 58.274
1.0515 "	1.832 "	" 57.396

The double potassium sulphate gave .265 grm. ThO_2, .156 grm. SO_3, and .3435 K_2SO_4. The SO_3, with the Berzelian atomic weights, represents .4537 grm. $BaSO_4$. Hence 100 $BaSO_4$ is equivalent to 58.408 ThO_2. This figure, combined with the two previous values for the same ratio, give a mean of 58.026, ± .214. Hence ThO_2 = 269.940, ± .997.

From the ratio between the K_2SO_4 and the ThO_2 in the double sulphate, ThO_2 = 268.284.

In 1861 new determinations were published by Chydenius,† whose memoir is accessible to me only in an abstract‡ which gives results without details. Thoria is regarded as a monoxide, ThO, and the old equivalents (O = 8) are used. The following values are assigned for the molecular weight of ThO, as found from analyses of several salts:

From Sulphate.	*From K. Th. Sulphate.*
66.33	67.02
67.13	
67.75	
68.03	
Mean, 67.252, ± .201	

* Poggend. Annal., 16, 398. 1829. Lehrbuch, 3, 1224.

† Kemisk undersökning af Thorjord och Thorsalter. Helsingfors, 1861. An academic dissertation.

‡ Poggend. Annal., 119, 55. 1863.

From Acetate.	*From Formate.*	*From Oxalate.*
67.31	68.06	65.87 } Two results
66.59	67.89	65.95 } by Berlin.
67.27	68.94	65.75
67.06		65.13
68.40	Mean, 68.297, $\pm$ .219	66.54
		65.85
Mean, 67.326, $\pm$ .201		
		Mean, 65.85, $\pm$ .123

We may fairly assume that these figures were calculated with O = 8, C = 6, and S = 16. Correcting by the values for these elements which have been found in previous chapters, ThO_2 becomes as follows:

From sulphate	ThO_2	= 268.584, $\pm$ .803
" acetate	"	= 268.735, $\pm$ .805
" formate	"	= 272.586, $\pm$ .877
" oxalate	"	= 262.804, $\pm$ .493

The single result from the double potassium sulphate is included with the column from the ordinary sulphate, and the influence of the atomic weight of potassium is ignored.

Chydenius was soon followed by Marc Delafontaine, whose researches appeared in 1863.* This chemist especially studied thorium sulphate; partly in its most hydrous form, partly as thrown down by boiling. In $Th(SO_4)_2.9H_2O$, the following percentages of ThO_2 were found:

45.08
44.90
45.06
45.21
45.06

Mean, 45.062, $\pm$ .0332

Hence ThO_2 = 263.637, $\pm$ .256.

The lower hydrate, $2Th(SO_4)_2.9H_2O$, was more thoroughly investigated. The thoria was estimated in two ways; first, (A,) by precipitation as oxalate and subsequent ignition; second, (B,) by direct calcination. These percentages of ThO_2 were found:

* Arch. des Sci. Phys. et Nat., (2,) 18, 343.

$$\left.\begin{array}{r} 52.83 \\ 52.52 \\ 52.72 \\ 52.13 \end{array}\right\} A.$$

$$\left.\begin{array}{r} 52.47 \\ 52.49 \\ 52.53 \\ 52.13 \\ 52.13 \\ 52.43 \\ 52.60 \\ 52.40 \\ 52.96 \\ 52.82 \end{array}\right\} B.$$

Mean, 52.511, ± .047

Hence ThO_2 = 266.025, ± .363.

In three experiments with this lower hydrate the sulphuric acid was also estimated, being thrown down as barium sulphate after removal of the thoria:

1.2425 grm. gave	.400 SO_3.	(1.1656 grm. $BaSO_4$.)	
1.138 "	.366 "	(1.0665 "	)
.734 "	.2306 "	(.6720 "	)

The figures in parenthesis are reproduced by myself from Delafontaine's results, he having calculated his analyses with O = 100, S = 200, and Ba = 857. These data may be reduced to a common standard, so as to represent the quantity of $2Th(SO_4)_2.9H_2O$ equivalent to 100 parts of $BaSO_4$. We then have the following results:

106.597
106.704
109.226

Mean, 107.509, ± .585

Hence ThO_2 = 259.555, ± 2.725.

Delafontaine seems himself to have calculated from the ratio between the percentages of SO_3 and ThO_2; whence, with our revised values for S, Ba, and O, ThO_2 = 262.643.

Delafontaine's work was soon confirmed by Hermann,*

* Journ. für Prakt. Chem., 93, 114.

who published a single analysis of the lower hydrated sulphate, as follows:

ThO_2	52.87
SO_3	32.11
H_2O	15.02
	100.00

Hence, from the ratio between SO_3 and ThO_2, ThO_2 = 263.030. Probably the SO_3 percentage was loss upon calcination.

The latest, and probably also the best determinations, are those of Cleve,* whose results, obtained from both the sulphate and the oxalate of thorium, agree admirably. The anhydrous sulphate, calcined, gave the subjoined percentages of thoria:

62.442
62.477
62.430
62.470
62.357
62.366

Mean, 62.423, ± .014

Hence ThO_2 = 265.380, ± .123.

The oxalate was subjected to a combustion analysis, whereby both thoria and carbonic acid could be estimated. From the direct percentages of these constituents no accurate value can be deduced, there having undoubtedly been moisture in the material studied. From the ratio between CO_2 and ThO_2, however, good results are attainable. This ratio I put in a fourth column, making the thoria proportional to 100 parts of carbon dioxide:

Oxalate.	*ThO_2.*	*CO_2.*	*Ratio.*
1.7135 grm.	1.0189 grm.	.6736 grm.	151.262
1.3800 "	.8210 "	.5433 "	151.114
1.1850 "	.7030 "	.4650 "	151.183
1.0755 "	.6398 "	.4240 "	150.896
		Mean,	151.114, ± .053

Hence ThO_2 = 265.357, ± .104.

* K. Svenska Vet. Akad. Handlinger. Bd. 2, No. 6. 1874.

There are now before us twelve estimates for the molecular weight of thoria. Two of these represent single experiments, and have no probable error attached to them; namely, the one due to Hermann, and the one deduced from Berzelius' $K_2SO_4 : ThO_2$ ratio. A third value, from Delafontaine's sulphuric acid estimations, has so high a probable error that it could be rejected without influencing the general mean. These three values might all be excluded without serious objection; but it is perhaps better to arbitrarily assign them equal weight, average them together, and give their mean the same probable error as that which attaches to Berzelius' $BaSO_4 : ThO_2$ series. This mean is indicated as "A" in the following combination:

Value "A"	ThO_2	$= 263.623, \pm .997$
Berzelius	"	$= 269.940, \pm .997$
Chydenius—Sulphate	"	$= 268.584, \pm .803$
" Acetate	"	$= 268.735, \pm .805$
" Formate	"	$= 272.586, \pm .877$
" Oxalate	"	$= 262.804, \pm .493$
Delafontaine—Higher hydrate	"	$= 263.637, \pm .256$
" Lower "	"	$= 266.025, \pm .363$
Cleve—Sulphate	"	$= 265.380, \pm .123$
" Oxalate	"	$= 265.357, \pm .104$
General mean	"	$= 265.341, \pm .072$

Hence Th $= 233.414, \pm .0725$; or, if O $= 16$, Th $= 233.951$.

These values vary from those derived from Cleve's experiments alone only in the second decimal.

GALLIUM.

Gallium has been so recently discovered, and obtained in such small quantities, that its atomic weight has not as yet been determined with much precision. The following data were fixed by the discoverer, Lecoq de Boisbaudran:*

* Journ. Chem. Soc., 1878, p. 646.

3.1044 grammes gallium ammonium alum, upon ignition, left .5885 grm. Ga_2O_3.

Hence Ga = 68.071. If O = 16, Ga = 68.233.

.4481 grammes gallium, converted into nitrate and ignited, gave .6024 grm. Ga_2O_3.

Hence Ga = 69.538. If O = 16, Ga = 69.693.

These values, assigned equal weight, give these means:

If O = 15.9633, Ga = 68.854. If O = 16, Ga = 68.963.

In brief, for all practical purposes, 69 may be assumed as the atomic weight of gallium.

INDIUM.

Reich and Richter, the discoverers of indium, were also the first to determine its atomic weight.* They dissolved weighed quantities of the metal in nitric acid, precipitated the solution with ammonia, ignited the precipitate, and ascertained its weight. Two experiments were made, as follows:

.5135 grm. indium	gave	.6243 grm.	In_2O_3.
.699	"	.8515	"

Hence, in mean, In = 110.61, if O = 16; a value known now to be too low.

An unweighed quantity of fresh, moist indium sulphide was also dissolved in nitric acid, yielding, on precipitation,

.2105 grm. In_2O_3 and .542 grm. $BaSO_4$.

Hence, with $BaSO_4$ = 233, In = 111.544; also too low.

Soon after the publication of Reich and Richter's paper the subject was taken up by Winkler.† He dissolved indium in nitric acid, evaporated to dryness, ignited the residue, and weighed the oxide thus obtained.

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* Journ. für Prakt. Chem., 92, 484.

† Journ. für Prakt. Chem., 94, 8.

.5574 grm. In gave	.6817 grm. In_2O_3.
.6661 "	.8144 "
.5011 "	.6126 "

Hence, in mean, if O = 16, In = 107.76; a result even lower than the values already cited.

In a later paper by Winkler* better results were obtained. Two methods were employed. First, metallic indium was placed in a solution of pure, neutral, sodio-auric chloride, and the amount of gold precipitated was weighed. I give the weighings and, in a third column, the amount of indium proportional to 100 parts of gold:

In.	*Au.*	*Ratio.*
.4471 grm.	.8205 grm.	57.782
.8445 "	1.4596 "	57.858
	Mean,	57.820, ± .026

Hence, if Au = 196.155, ± .095, In = 113.417, ± .074.

Winkler also repeated his earlier process, converting indium into oxide by solution in nitric acid and ignition of the residue. An additional experiment, the third as given below, was made after the method of Reich and Richter. The third column gives the percentage of In in In_2O_3:

1.124 grm. In gave	1.3616 grm. In_2O_3.	Per cent., 82.550
1.015 "	1.2291 "	" 82.581
.6376 "	.7725 "	" 82.537

These figures were confirmed by a single experiment of Bunsen's,† published simultaneously with the specific heat determinations which showed that the oxide of indium was In_2O_3, and not InO as had been previously supposed:

1.0592 grm. In gave 1.2825 grm. In_2O_3. Per cent. In, 82.589

For convenience we may add this figure in with Winkler's series, which gives us a mean percentage of In in In_2O_3 of 82.564, ± .0082. Hence, if O = 15.9633, ± .0035, In = 113.385, ± .060.

* Journ. für Prakt. Chem., 102, 282.

† Poggend. Annal., 141, 28.

Combining results, we have the following general mean:

From gold series	In	= 113.417, ± .074
" oxide "	"	= 113.385, ± .060
General mean	"	= 113.398, ± .047

Or, if O = 16, In = 113.659.

CERIUM.

Although cerium was discovered almost at the beginning of the present century, its atomic weight was not properly determined until after the discovery of lanthanum and didymium by Mosander. In 1842 the investigation was undertaken by Beringer,* who employed several methods. His cerium salts, however, were all rose-colored, and therefore were not wholly free from didymium; and his results are further affected by a negligence on his part to fully describe his analytical processes.

First, a neutral solution of cerium chloride was prepared by dissolving the carbonate in hydrochloric acid. This gave weights of ceroso-ceric oxide and silver chloride as follows. The third column shows the amount of CeO_2 proportional to 100 parts of AgCl:

CeO_2.	*AgCl.*	*Ratio.*
.5755 grm.	1.419 grm.	40.557
.6715 "	1.6595 "	40.464
1.1300 "	2.786 "	40.560
.5366 "	1.3316 "	40.297
		Mean, 40.469, ± .0415

The analysis of the dry cerium sulphate gave results as follows. In a fourth column I show the amount of CeO_2 proportional to 100 parts of $BaSO_4$:

* Ann. Chem. Pharm., 42, 134.

Sulphate.	*CeO_2.*	*$BaSO_4$.*	*Ratio.*
1.379 grm.	.8495 grm.	1.711 grm.	49.649
1.276 "	.7875 "	1.580 "	49.836
1.246 "	.7690 "	1.543 "	49.838
1.553 "	.9595 "	1.921 "	49.948
			Mean, 49.819, ± .042

Beringer also gives a single analysis of the formate and the results of one conversion of the sulphide into oxide. The figures are, however, not valuable enough to cite.

The foregoing data involve one variation from Beringer's paper. Where I put CeO_2 as found he puts Ce_2O_3. The latter is plainly inadmissible, although the atomic weights calculated from it agree curiously well with some other determinations. For instance, in the chloride series, the assumption of Ce_2O_3 as the formula of the oxide obtained, gives Ce = 137.749, while CeO_2 makes Ce = 141.636. The former agrees with the results of Wolf, Wing, and others quite fairly; the latter is near the value obtained by Bührig. Obviously, the presence of didymium in the salts analyzed should tend to raise rather than to lower the apparent atomic weight of cerium.

Shortly after Beringer, Hermann* published the results of one experiment. 23.532 grm. of anhydrous cerium sulphate gave 29.160 grm. of $BaSO_4$. Hence 100 parts of the sulphate correspond to 123.926 of $BaSO_4$.

In 1848 similar figures were published by Marignac,† who found the following amounts of $BaSO_4$ proportional to 100 of dry cerium sulphate:

122.68
122.00
122.51

Mean, 122.40, ± .138

If we give Hermann's single result the weight of one experiment in this series, and combine, we get a mean value of 123.019, ± .113.

* Journ. für Prakt. Chem., 30, 185. 1843.
† Arch. des Sciences Phys. et Nat., (1,) 8, 273. 1848.

Still another method was employed by Marignac. A definite mixture was made of solutions of cerium sulphate and barium chloride. To this were added, volumetrically, solutions of each salt successively, until equilibrium was attained. The figures published give maxima and minima for the $BaCl_2$ proportional to each lot of $Ce_2(SO_4)_3$. In another column, using the mean value for $BaCl_2$ in each case, I put the ratio between 100 parts of this salt and the equivalent quantity of sulphate. The latter compound was several times recrystallized:

	$Ce_2(SO_4)_3$.	$BaCl_2$.	*Ratio.*
First crystallization	11.011 grm.	11.990 — 12.050 grm.	91.606
" "	13.194 "	14.365 — 14.425 "	91.657
Second "	13.961 "	15.225 — 15.285 "	91.518
" "	12.627 "	13.761 — 13.821 "	91.559
" "	11.915 "	12.970 — 13.030 "	91.654
Third "	14.888 "	16.223 — 16.283 "	91.602
" "	14.113 "	15.383 — 15.423 "	91.755
Fourth "	13.111 "	14.270 — 14.330 "	91.685
" "	13.970 "	15.223 — 15.283 "	91.588

Mean, 91.625, ± .016

Omitting the valueless experiments of Kjerulf,* we come next to the figures published by Bunsen and Jegel † in 1858. From the air dried sulphate of cerium the metal was precipitated as oxalate, which, ignited, gave CeO_2. In the filtrate from the oxalate the sulphuric acid was estimated as $BaSO_4$:

1.5726 grm. sulphate gave .7899 grm. CeO_2 and 1.6185 grm. $BaSO_4$.
1.6967 " .8504 " 1.7500 "

Hence, for 100 parts $BaSO_4$, the CeO_2 is as follows:

48.804
48.575

Mean, 48.689, ± .077

One experiment was also made upon the oxalate:

.3530 grm. oxalate gave .1913 CeO_2 and .0506 H_2O.

Hence, in the dry salt, we have 63.261 per cent. of CeO_2.

* Ann. Chem. Pharm., 87, 12.
† Ann. Chem. Pharm., 105, 45.

In each sample of CeO_2 the excess of oxygen over true Ce_2O_3 was estimated by an iodometric titration; but the data thus obtained need not be further considered.

In two papers by Rammelsberg* data are given for the atomic weight of cerium, as follows. In the earlier paper cerium sulphate is analyzed, the cerium being thrown down by caustic potash, and the acid precipitated from the filtrate as barium sulphate:

.413 grm. $Ce_2(SO_4)_3$ gave .244 grm. CeO_2 and .513 grm $BaSO_4$.

Hence 100 $BaSO_4$ = 47.563 CeO_2, a value which may be combined with others, thus; this figure being assigned a weight equal to one experiment in Bunsen's series:

Beringer	49.819, ± .042
Bunsen and Jegel	48.689, ± .077
Rammelsberg	47.563, ± .108
General mean	49.360, ± .035

It should be noted here that this mean is somewhat arbitrary, since Bunsen and Rammelsberg's cerium salts were undoubtedly freer from didymium than the material studied by Beringer.

In his later paper Rammelsberg gives these figures concerning cerium oxalate. 100 parts gave 10.43 of carbon and 21.73 of water. Hence the dry salt should yield 48.862 per cent. of CO_2, whence Ce = 137.83.

In all of the foregoing experiments the ceroso-ceric oxide was somewhat colored, the tint ranging from one shade to another of light brown according to the amount of didymium present. Still, at the best, a faint color remained, which was supposed to be characteristic of the oxide itself. In 1868, however, some experiments of Dr. C. Wolf† were posthumously made public, which went to show that pure ceroso-ceric oxide is white, and that all samples previously studied were contaminated with some other earth, not necessarily didymium but possibly a new substance, the removal of

* Poggend. Annal., 55, 65; 108, 44.

† Amer. Journ. Science and Arts, (2,) 46, 53.

which tended to lower the apparent atomic weight of cerium very perceptibly.

Cerium sulphate was recrystallized at least ten times. Even after twenty recrystallizations it still showed spectroscopic traces of didymium. The water contained in each sample of the salt was cautiously estimated, and the cerium was thrown down by boiling concentrated solutions of oxalic acid. The resulting oxalate was ignited with great care. I deduce from the weighings the percentage of CeO_2 given by the *anhydrous* sulphate:

Sulphate.	*Water.*	*CeO_2.*	*Per cent. CeO_2.*
1.4542 grm.	.19419 grm.	.76305 grm.	60.559
1.4104 "	.1898 "	.7377 "	60.437
1.35027 "	.1820 "	.70665 "	60.487
			Mean, 60.494, ± .024

After the foregoing experiments the sulphate was further purified by solution in nitric acid and pouring into a large quantity of boiling water. The precipitate was converted into sulphate and analyzed as before:

Sulphate.	*Water.*	*CeO_2.*	*Per cent. CeO_2.*
1.4327 grm.	.2733 grm.	.69925 grm.	60.311
1.5056 "	.2775 "	.7405 "	60.296
1.44045 "	.2710 "	.7052 "	60.300
			Mean, 60.302, ± .004

From another purification the following weights were obtained:

1.4684 grm.	.1880 grm.	.7717 grm.	60.270 per cent.

A last purification gave a still lower percentage:

1.3756 grm.	.1832 grm.	.7186 grm.	60.265 per cent.

The last oxide was perfectly white, and was spectroscopically free from didymium. In each case the CeO_2 was titrated iodometrically for its excess of oxygen. It will be noticed that in the successive series of determinations the percentage of CeO_2 steadily and strikingly diminishes, to an extent for which no ordinary impurity of didymium can

account. The death of Dr. Wolf interrupted the investigation, the results of which were edited and published by Professor F. A. Genth.

The experiments of Wolf seem to have hitherto escaped general notice, except from Wing, who has partially verified them.* This chemist, incidentally to other researches, purified some cerium sulphate after the method of Wolf, and made two similar analyses of it, as follows:

Sulphate.	*Water.*	*CeO_2.*	*Per cent. CeO_2.*
1.2885 grm.	.1707 grm.	.6732 grm.	60.225
1.4090 "	.1857 "	.7372 "	60.263
		Mean,	60.244, ± .012

The ceroso-ceric oxide in this case was perfectly white. The cerium oxalate which yielded it was precipitated boiling by a boiling concentrated solution of oxalic acid. The precipitate stood twenty-four hours before filtering.

We may now combine the results of Wolf and of Wing, as follows. The two concordant experiments of Wolf's series three and four may be united, giving a mean of 60.267, ± .001:

Wolf, 1st series	60.494, ± .024
" 2d "	60.302, ± .004
" 3d and 4th series	60.267, ± .001
Wing	60.244, ± .012
General mean	60.271, ± .001

This mean, the percentage of CeO_2 in the anhydrous sulphate, gives Ce = 137.724; or, if O = 16, Ce = 138.039. This varies widely from the ordinarily accepted value as determined by Buehrig.

In 1875 Buehrig's† paper upon the atomic weight of cerium was issued. He first studied the sulphate, which, after eight crystallizations, still retained traces of free sulphuric acid. He found furthermore that the salt obstinately retained traces of water, which could not be wholly expelled by heat without partial decomposition of the material.

* Amer. Journ. Sci. and Arts, (2.) 49, 358. 1870.

† Journ. für Prakt. Chem., 120, 222.

These sources of error probably affect all the previously cited series of experiments; although, in the case of Wolf's work, it is doubtful whether they could have influenced the atomic weight of cerium by more than one or two tenths of a unit. Buehrig also found, as Marignac had earlier shown, that upon precipitation of cerium sulphate with barium chloride the barium sulphate invariably carried down traces of cerium. Furthermore, the ceroso-ceric oxide from the filtrate always contained barium. For these reasons the sulphate was abandoned, and the atomic weight determinations of Buehrig were made with air-dried oxalate. This salt was placed in a series of platinum boats in a combustion tube behind copper oxide. It was then burned in a stream of pure, dry oxygen, and the carbonic acid and water were collected after the usual method. Ten experiments were made; in all of them the above named products were estimated, and in five analyses the resulting ceroso-ceric oxide was also weighed. By deducting the water found from the weight of the air-dried oxalate, the weight of the anhydrous oxalate is obtained, and the percentages of its constituents are easily determined. In weighing, the articles weighed were always counterpoised with similar materials. The following weights were found:

Oxalate.	*Water.*	*CO_2.*	*CeO_2.*
9.8541 grm.	2.1987 grm.	3.6942 grm.	------
9.5368 "	2.1269 "	3.5752 "	------
9.2956 "	2.0735 "	3.4845 "	------
10.0495 "	2.2364 "	3.7704 "	------
10.8249 "	2.4145 "	4.0586 "	------
9.3679 "	2.0907 "	3.5118 "	4.6150 grm.
9.7646 "	2.1769 "	3.6616 "	4.8133 "
9.9026 "	2.2073 "	3.7139 "	4.8824 "
9.9376 "	2.2170 "	3.7251 "	4.8971 "
9.5324 "	2.1267 "	3.5735 "	4.6974 "

These figures give us the following percentages for CO_2 and CeO_2 in the anhydrous oxalate:

CO_2.	*CeO_2.*
48.256	------
48.249	------
48.248	------

CeO_2.	CO_2.
48.257	------
48.257	------
48.258	63.417
48.257	63.436
48.262	63.446
48.249	63.429
48.253	63.430
Mean, 48.2546, ± .001	63.4316, ± .0032

From percentage CO_2 ------ Ce = 141.228, ± .025
" CeO_2 ----- " = 141.141, ± .020

Obviously the single oxalate experiments of Jegel and of Rammelsberg would exert no appreciable influence upon these mean results. They may therefore be ignored.

In combining all of these data in one general mean, we may begin as usual by tabulating our ratios:

(1.) $BaSO_4 : Ce_2(SO_4)_3 :: 100 : 123.019, \pm .113$
(2.) $BaSO_4 : CeO_2 :: 100 : 49.360, \pm .035$
(3.) $BaCl_2 : Ce_2(SO_4)_3 :: 100 : 91.625, \pm .016$
(4.) $AgCl : CeO_2 :: 100 : 40.469, \pm .0415$
(5.) Percentage CeO_2 from anhydrous sulphate, 60.271, ± .001
(6.) " " " oxalate, 63.4316, ± .0032
(7.) " CO_2 " " 48.2546, ± .001

These ratios give us four values for the molecular weight of CeO_2 and two values for $Ce_2(SO_4)_3$:

From (2)---------------CeO_2 = 172.218, ± .124
" (4)--------------- " = 173.663, ± .179
" (5)--------------- " = 169.651, ± .034
" (6)--------------- " = 173.068, ± .033

General mean----- " = 171.490, ± .023

From (1)-----------$Ce_2(SO_4)_3$ = 567.234, ± .522
" (3)----------- " = 570.375, ± .165

General mean " = 570.093, ± .156

Hence we have three independent values for the atomic weight of cerium, as follows:

From molecular weight of CeO_2	Ce	$= 139.563, \pm .024$
" " $Ce_2(SO_4)_3$	"	$= 141.281, \pm .083$
From ratio (7,) CO_2 in oxalate	"	$= 141.228, \pm .025$
General mean	"	$= 140.424, \pm .017$

Or, if O = 16, Ce = 140.747.

Buehrig's results alone, both sets combined, give Ce = 141.198, ± .020; or, if O = 16, Ce = 141.523.

Wolf and Wing's figures alone make Ce = 137.724; or, if O = 16, Ce = 138.039.

The latter result is subject to the errors pointed out by Buehrig as involved in the use of cerium sulphate; but the ceroso-ceric oxide obtained in the analyses was pure white. Buehrig's ceroso-ceric oxide, on the other hand, was yellow. In neither case was didymium present. All things considered, therefore, it is probable that the lower result is too low and the higher result too high. How near the general mean of all may be to the truth we have no evidence to show. It is clear that new determinations are needed, made with material yielding *white* ceroso-ceric oxide, and with avoidance of the sources of error which Buehrig pointed out.

LANTHANUM.

Leaving out of account the work of Mosander, and the valueless experiments of Choubine, we may consider the estimates of the atomic weight of lanthanum which are due to Hermann, Rammelsberg, Marignac, Czudnowicz, Holzmann, Zschiesche, Erk, and Cleve.

From Rammelsberg* we have but one analysis. .700 grm. of lanthanum sulphate gave .883 grm. of barium sulphate. Hence 100 parts of $BaSO_4$ are equivalent to 79.276 of $La_2(SO_4)_3$.

* Poggend. Annal., 55, 65.

Marignac,* working also with the sulphate of lanthanum, employed two methods. First, the salt in solution was mixed with a slight excess of barium chloride. The resulting barium sulphate was filtered off and weighed; but, as it contained some occluded lanthanum compounds, its weight was too high. In the filtrate the excess of barium was estimated, also as sulphate. This last weight of sulphate, deducted from the total sulphate which the whole amount of barium chloride could form, gave the sulphate actually proportional to the lanthanum compound. The following weights are given:

$La_2(SO_4)_3$.	$BaCl_2$.	1st $BaSO_4$.	2d $BaSO_4$.
4.346 grm.	4.758 grm.	5.364 grm.	.115 grm.
4.733 "	5.178 "	5.848 "	.147 "

Hence we have the following quantities of $La_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$. Column A is deduced from the first $BaSO_4$ and column B from the second, after the manner above described:

A.	B.
81.022	83.281
80.934	83.662
Mean, 80.978, ± .030	Mean, 83.471, ± .128

From A..........................La = 138.776
" B.......................... " = 147.474

A agrees best with other determinations, although, theoretically, it is not so good as B.

Marignac's second method, described in the same paper with the foregoing experiments, consisted in mixing solutions of $La_2(SO_4)_3$ with solutions of $BaCl_2$, titrating one with the other until equilibrium was established. The method has already been described under cerium. The weighings give maxima and minima for $BaCl_2$. In another column I give $La_2(SO_4)_3$ proportional to 100 parts of $BaCl_2$, mean weights being taken for the latter:

* Archives des Sci Phys. et Naturelles, (1,) 11, 29. 1849.

$La_2(SO_4)_3$.	$BaCl_2$.	Ratio.
11.644 grm.	12.765 — 12.825 grm.	91.004
12.035 "	13.195 — 13.265 "	90.968
10.690 "	11.669 — 11.749 "	91.297
12.750 "	13.920 — 14.000 "	91.332
10.757 "	11.734 — 11.814 "	91.362
12.672 "	13.813 — 13.893 "	91.475
9.246 "	10.080 — 10.160 "	91.364
10.292 "	11.204 — 11.264 "	91.615
10.192 "	11.111 — 11.171 "	91.482
		Mean, 91.322, ± .048

Hence La = 140.484.

Although not next in chronological order, some still more recent work of Marignac's* may properly be considered here. The salt studied was the sulphate of lanthanum, purified by repeated crystallizations. In two experiments the salt was calcined, and the residual oxide weighed; in two others the lanthanum was precipitated as oxalate, and converted into oxide by ignition. The following percentages are given for La_2O_3:

57.56 } By calcination.
57.58 }
57.50 } Ppt. as oxalate.
57.55 }

Mean, 57.5475, ± .0115

The atomic weight determinations of Holzmann† were made by analyses of the sulphate and iodate of lanthanum, and the double nitrate of magnesium and lanthanum. In the sulphate experiments the lanthanum was first thrown down as oxalate, which, on ignition, yielded oxide. The sulphuric acid was precipitated as $BaSO_4$ in the filtrate.

$La_2(SO_4)_3$.	La_2O_3.	$BaSO_4$.
.9663 grm.	.5157 grm.	1.1093 grm.
.6226 "	.3323 "	.7123 "
.8669 "	.4626 "	.9869 "

* Ann. de Chim. et de Phys., (4,) 30, 68. 1873.
† Journ. für Prakt. Chem., 75, 321. 1858.

These results are best used by taking the ratio between the $BaSO_4$, put at 100, and the La_2O_3. The figures are then as follows:

46.489
46.652
46.873

Mean, 46.671, ± .075

In the analyses of the iodate the lanthanum was thrown down as oxalate, as before. The iodic acid was also estimated volumetrically, but the figures are hardly available for present discussion. The following percentages of La_2O_3 were found:

23.454
23.419
23.468

Mean, 23.447, ± .0216

The formula of this salt is $La_2(IO_3)_6.3H_2O$.

The double nitrate, $La_2(NO_3)_6.3Mg(NO_3)_2.24H_2O$, gave the following analytical data:

Salt.	*H_2O.*	*MgO.*	*La_2O_3.*
.5327 grm.	.1569 grm.	.0417 grm.	.1131 grm.
.5931 "	.1734 "	.0467 "	.1262 "
.5662 "	.1647 "	.0442 "	.1197 "
.3757 "	------	.0297 "	.0813 "
.3263 "	------	.0256 "	.0693 "

These weighings give the subjoined percentages of La_2O_3:

21.231
21.278
21.141
21.640
21.238

Mean, 21.3056, ± .058

These data of Holzmann give values for the molecular weight of La_2O_3 as follows:

From sulphate	La_2O_3	= 325.674, ± .522
" iodate	"	= 322.419, ± .113
" magnesian nitrate	"	= 324.355, ± .923

Czudnowicz* based his determination of the atomic weight of lanthanum upon one analysis of the air-dried sulphate. The salt contained 22.741 per cent. of water.

.598 grm. gave .272 grm. La_2O_3 and .586 grm. $BaSO_4$.

The La_2O_3 was found by precipitation as oxalate and ignition. The $BaSO_4$ was thrown down from the filtrate. Reduced to the standards already adopted these data give for the percentage of La_2O_3 in the anhydrous sulphate the figure 58.668. 79.117 parts of the salt are proportional to 100 parts of $BaSO_4$.

Hermann† studied both the sulphate and the carbonate of lanthanum. From the anhydrous sulphate, by precipitation as oxalate and ignition, the following percentages of La_2O_3 were obtained:

57.690
57.663
57.610

Mean, 57.654, $\pm$ .016

The carbonate, dried at 100°, gave the following percentages:

68.47 La_2O_3.
27.67 CO_2.
3.86 H_2O.

Reckoning from the ratio between CO_2 and La_2O_3 the molecular weight of the latter becomes 325.896.

Zschiesche's‡ experiments consist of six analyses of lanthanum sulphate, which salt was dehydrated at 230°, and afterwards calcined. I subjoin his percentages, and in a fourth column deduce from them the percentage of La_2O_3 in the *anhydrous* salt:

H_2O.	SO_3.	La_2O_3.	La_2O_3 *in anhydrous salt.*
22.629	33.470	43.909	56.745
22.562	33.306	44.132	56.964
22.730	33.200	44.070	57.034

* Journ. für Prakt. Chem., 80, 33. 1860.
† Journ. für Prakt. Chem., 82, 396. 1861.
‡ Journ. für Prakt. Chem., 104, 174.

H_2O.	SO_3.	La_2O_3.	La_2O_3 *in anhydrous salt.*
22.570	33.333	44.090	56.947
22.610	33.160	44.240	57.150
22.630	33.051	44.310	57.277
			Mean, 57.021, ± .051

Erk * found that .474 grm. of $La_2(SO_4)_3$, by precipitation as oxalate and ignition, gave .2705 grm. of La_2O_3, or 57.068 per cent. .7045 grm. of the sulphate also gave .8815 grm. of $BaSO_4$. Hence 100 parts of $BaSO_4$ are equivalent to 79.921 of $La_2(SO_4)_3$.

Last of all, and probably best of all, we come to the determinations of Cleve.† Strongly calcined La_2O_3, spectroscopically pure, was dissolved in nitric acid, and then, by evaporation with sulphuric acid, converted into sulphate:

1.9215 grm. La_2O_3 gave	3.3365 grm. sulphate.	57.590 per cent.
2.0570 "	3.5705 "	57.611 "
1.6980 "	2.9445 "	57.667 "
2.0840 "	3.6170 "	57.617 "
1.9565 "	3.3960 "	57.612 "
		Mean, 57.619, ± .0085

From the last column, which indicates the percentage of La_2O_3 in $La(SO_4)_3$, we get, if $SO_3 = 80$, La = 139.15.

We may now combine the similar means into general means, and deduce a value for the atomic weight of lanthanum. For the percentage of oxide in sulphate we have six estimates, as follows. The single experiments of Czudnowicz and of Erk are assigned the probable error and weight of a single experiment in Hermann's series:

Czudnowicz	58.668, ± .027
Erk	57.068, ± .027
Hermann	57.654, ± .016
Zschiesche	57.021, ± .051
Marignac	57.5475, ± .0115
Cleve	57.619, ± .0085
General mean	57.620, ± .0059

* Jenaisches' Zeitschrift, 6, 306. 1871.

† K. Svenska Vet. Akad. Handlingar, Bd. 2, No. 7. 1874.

For the quantity of $La_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$, we have five experiments, which may be given equal weight and averaged together:

Marignac	81.022
"	80.934
Rammelsberg	79.276
Czudnowicz	79.117
Erk	79.921
Mean,	80.054, $\pm$ .270

In all, there are seven ratios from which to calculate:

(1.) Percentage of La_2O_3 in $La_2(SO_4)_3$, 57.620, $\pm$ .0059
(2.) $BaCl_2 : La_2(SO_4)_3 :: 100 : 91.322$, $\pm$ .048—Marignac.
(3.) $BaSO_4 : La_2(SO_4)_3 :: 100 : 80.054$, $\pm$ .270
(4.) $BaSO_4 : La_2O_3 :: 100 : 46.671$, $\pm$ .075—Holzmann.
(5.) Percentage of La_2O_3 in iodate, 23.447, $\pm$ .0216—Holzmann.
(6.) " " magnesian nitrate, 21.3056, $\pm$ .058—Holzmann.
(7.) " " carbonate, 68.47—Hermann.

These ratios give five values for the molecular weight of lanthanum oxide, and two for that of the sulphate:

From (2)	$La_2(SO_4)_3$	= 568.488, $\pm$ .320
" (3)	"	= 558.624, $\pm$ 1.888
General mean,	"	= 568.212, $\pm$ .316

Hence La = 140.346, $\pm$ .160.

From (1)	La_2O_3	= 325.791, $\pm$ .074
" (4)	"	= 325.674, $\pm$ .522
" (5)	"	= 322.419, $\pm$ .113
" (6)	"	= 324.355, $\pm$ .923
" (7)	"	= 325.896, $\pm$ .488
General mean	"	= 324.810, $\pm$ .061

Here the value derived from ratio (7) is given the weight of a single experiment in ratio (1.) Hence La = 138.460, $\pm$ .031.

Combining the two values for La, we get this final result:

From La_2O_3	La	= 138.460, $\pm$ .031
" $La_2(SO_4)_3$	"	= 140.346, $\pm$ .160
General mean	"	= 138.526, $\pm$ .030

Or, if O = 16, La = 138.844.

Since this value is a little under and Cleve's a little over 139, the latter figure may fairly be used in all calculations involving a knowledge of the atomic weight of lanthanum.

DIDYMIUM.

The atomic weight of didymium has been determined by Marignac, Hermann, Zschiesche, Erk, and Cleve. Mosander's early experiments we may leave out of account.

Marignac* mixed a solution of the sulphate with a slight excess of barium chloride, filtered, weighed the precipitate, and estimated the excess of barium in the filtrate by the ordinary method. The first precipitate always contained didymium, and therefore weighed too much. By deducting the weight of the second precipitate, representing the excess of the barium chloride, from the weight of barium sulphate theoretically formable, the weight of the latter proportional to the quantity of didymium salt taken was found:

$Di_2(SO_4)_3$.	$BaCl_2$.	1st $BaSO_4$.	2d $BaSO_4$.
3.633 grm.	3.902 grm.	4.412 grm.	.084 grm.
3.862 "	4.227 "	4.679 "	.075 "
3.330 "	3.552 "	4.027 "	.088 "
1.386 "	1.477 "	1.681 "	.014 "

These figures give us a ratio between the sulphates of didymium and barium which we may express as follows. Column A gives the $Di_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$, as calculated from the first precipitate of the latter. Column B gives a similar ratio calculated with the second $BaSO_4$ precipitate, this being deduced from the total $BaSO_4$ which the chloride used could form:

A.	B.
82.344	84.685
82.539	82.626
82.692	85.545
82.451	84.425
82.247—Erk.	
	Mean, 84.320, ± .414
Mean, 82.455, ± .052	

* Arch. des Sci. Phys. et Naturelles, (1,) 11, 29. 1849.

To A I have added a single result of Erk's, to be described further along. It will be seen that although A is theoretically defective, its figures are much more concordant than those in B. In fact, the latter would almost vanish for the final general mean for the atomic weight of didymium:

From A	Di = 143.929
" B	" = 150.436

In a later paper* Marignac adopts two other methods for establishing the atomic weight of didymium. The carefully dehydrated sulphate was taken, the didymium was precipitated as oxalate, and the latter, ignited, yielded oxide. The following percentages of oxide were found:

58.22
58.24
58.29
58.31
58.29

Mean, 58.27, ± .0115

The chloride of didymium was also studied. As the anhydrous salt could not be obtained in an absolutely definite state, Marignac prepared neutral solutions of it and determined the ratio between didymium oxide and silver chloride. The latter compound was first precipitated in the usual way, and filtered off; the excess of silver in the filtrate was removed by hydrochloric acid, and after that the didymium was thrown down as oxalate and weighed as oxide. The subjoined weights of AgCl and Di_2O_3 were found. In a third column I give the ratio between the two compounds, putting AgCl at 100:

AgCl.	*Di_2O_3.*	*Ratio.*
10.058 grm.	3.946 grm.	39.232
5.029 "	1.960 "	38.974
5.844 "	2.276 "	38.946
		Mean, 39.051, ± .061

Hence Di = 143.637, ± .263.

* Ann. d. Chim. et d. Phys., (3,) 38, 148. 1853.

Hermann's* determination of the atomic weight of didymium rests on a single experiment with the sulphate. By precipitation as oxalate and subsequent ignition, he found that this salt yielded 58.14 per cent. of Di_2O_3.

Zschiesche† also analyzed didymium sulphate, which he dehydrated at 230°, and afterwards converted into oxide by calcination. I give his percentages, and also, in a fourth column, the percentage of oxide from the *anhydrous* sulphate as deduced from his figures:

H_2O.	SO_3.	Di_2O_3.	Di_2O_3 *in anhyd. salt.*
23.19	32.97	43.83	57.070
23.03	32.39	44.58	57.919
23.00	32.56	44.95	58.006
23.547	31.938	44.515	58.225
22.550	32.870	44.570	57.554

The salt used in the first experiment probably contained lanthanum. Rejecting this, the mean of the figures remaining in the fourth column is 57.926, ± .094. Hence Di = 141.007.

Erk,‡ to whom reference has already been made, estimated didymium in the sulphate by precipitation as oxalate and calcination to oxide:

$Di_2(SO_4)_3$	Di_2O_3.	*Per cent.* Di_2O_3.
.556 grm.	.323 grm.	58.094
.674 "	.3915 "	58.087

Hermann's single result for this percentage, 58.14, agrees more nearly with Erk's series than with any other. It may therefore be averaged in with Erk's two experiments, giving a mean of 58.107, ± .0112. Erk also obtained from .7065 grm. of sulphate .859 grm. $BaSO_4$. This experiment has already been averaged with Marignac's earlier results.

The latest determinations of the atomic weight of didymium were published by Cleve‖ in 1874. Strongly calcined

* Journ. für Prakt. Chem., 82. 367. 1861.

† Journ. für Prakt. Chem., 107, 74.

‡ Jenaisches' Zeitschrift, 6, 306. 1871.

‖ K. Svenska Vet. Akad. Handlingar, Bd. 2, No. 8. These figures were kindly transcribed for me by Professor Delafontaine of Chicago, as I had not access to a copy of the original memoir.

didymium oxide was dissolved in nitric acid, the solution was evaporated with sulphuric acid, and the weight of the resulting sulphate was ascertained. I subjoin the weighings and the percentage of Di_2O_3 in $Di_2(SO_4)_3$:

Di_2O_3.	$Di_2(SO_4)_3$.	*Per cent.* Di_2O_3.
2.257 grm.	3.844 grm.	58.715
1.086 "	1.8485 "	58.750
1.1525 "	1.9615 "	58.756
1.3635 "	2.319 "	58.797
1.9655 "	3.3435 "	58.786
1.528 "	2.599 "	58.792
		Mean, 58.766, ± .0087

Hence Di = 146.804. If SO_3 = 80, Di = 147.021.

This determination is undoubtedly the best of all, and might properly be accepted to the exclusion of the others. Still, it is worth while to combine all the figures into one general mean. For the percentage of Di_2O_3 in $Di_2(SO_4)_3$ we have the following data:

Marignac	58.270, ± .0115
Erk and Hermann	58.107, ± .0112
Zschiesche	57.926, ± .094
Cleve	58.766, ± .0087
General mean	58.451, ± .0059

For the atomic weight of didymium we have now three independent values:

From per cent. Di_2O_3 in $Di_2(SO_4)_3$	Di = 144.604, ± .031
" Marignac's chloride analyses	" = 143.637, ± .263
" Marignac's and Erk's $BaSO_4$ ratio	" = 143.929, ± .189
General mean	" = 144.573, ± .0306

If O = 16, Di = 144.906.

THE YTTRIUM GROUP.

The atomic weights of the metals in this group can only be said to have been determined approximately. Not only do great difficulties attend the purification of the material used for study and the separation of the earths from each other, but there have been and still are grave doubts as to the actual nature of some of the latter. The figures for scandium, yttrium, and ytterbium seem to be tolerably good; those for decipium, philippium, thulium, erbium, and terbium are little more than estimates; for samarium we have no data whatever. All the atomic weights in this group are based upon analyses or syntheses of sulphates; and from analogy to the cerium metals all of these elements are regarded as forming sesquioxides.

SCANDIUM.

Cleve,* who was the first to make accurate experiments on the atomic weight of this metal, obtained the following data. 1.451 grm. of sulphate, ignited, gave .5293 grm. of Sc_2O_3. .4479 grm. of Sc_2O_3, converted into sulphate, yielded 1.2255 grm. of the latter, which, upon ignition, gave .4479 grm. of Sc_2O_3. Hence, for the percentage of Sc_2O_3 in $Sc_2(SO_4)_3$ we have:

36.478
36.556
36.556

Mean, 36.530

Hence, if $SO_3 = 80$, $Sc = 45.044$.

Later and better results are those of Nilson,† who converted scandium oxide into the sulphate. I give in a third column the percentage of oxide in sulphate:

* Compt. Rend., 89, 419.
† Compt. Rend., 91, 118.

.3379 grm. Sc_2O_3 gave	.9343 grm. $Sc_2(SO_4)_3$.		36.166 per cent.
.3015 "	.8330	"	36.194 "
.2998 "	.8257	"	36.187 "
.3192 "	.8823	"	36.178 "
			Mean, 36.181, ± .004

Hence Sc = 43.980, ± .015: or, if O = 16, then Sc = 44.081. If SO_3 = 80, then Sc = 44.032. These values are doubtless very nearly correct.

YTTRIUM.

For yttrium we need consider only the determinations of Popp, Delafontaine, Bahr and Bunsen, and Cleve.

Popp* evidently worked with material not wholly free from earths of higher molecular weight than yttria. The yttrium sulphate was dehydrated at 200°; the sulphuric acid was then estimated as barium sulphate; and after the excess of barium in the filtrate had been removed, the yttrium was thrown down as oxalate, and ignited to yield oxide. The following are the weights given by Popp:

Sulphate.	*$BaSO_4$.*	*Yt_2O_3.*	*H_2O.*
1.1805 grm.	1.3145 grm.	.4742 grm.	.255 grm.
1.4295 "	1.593 "	.5745 "	.308 "
.8455 "	.9407 "	.3392 "	.1825 "
1.045 "	1.1635 "	.4195 "	.2258 "

Eliminating water, these figures give us for the percentages of Yt_2O_3 in $Yt_2(SO_4)_3$ the values in column A. In column B I put the quantities of Yt_2O_3 proportional to 100 parts of $BaSO_4$:

A.	B.
51.237	36.075
51.226	36.064
51.161	36.058
51.209	36.055
Mean, 51.208, ± .011	Mean, 36.063, ± .003

From B, Yt = 101.880. The values in A will be combined with similar data from other experimenters.

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* Ann. Chem. Pharm., 131, 179.

In 1865 Delafontaine* published some results obtained from yttrium sulphate, the yttrium being thrown down as oxalate and weighed as oxide. In the fourth column I give the percentages of Yt_2O_3 reckoned from the anhydrous sulphate:

Sulphate.	Yt_2O_3.	H_2O.	*Per cent.* Yt_2O_3.
.9545 grm.	.371 grm.	.216 grm.	50.237
2.485 "	.9585 "	.565 "	49.922
2.153 "	.827 "	.4935 "	49.834

Mean, 49.998, ± .081

In another paper† Delafontaine gives the following percentages of Yt_2O_3 in dry sulphate. The mode of estimation was the same as before:

48.23
48.09
48.37

Mean, 48.23, ± .055

Bahr and Bunsen,‡ and likewise Cleve, adopted the method of converting dry yttrium oxide into anhydrous sulphate, and noting the gain in weight. Bahr and Bunsen give us the two following results. I add the usual percentage column:

Yt_2O_3.	$Yt_2(SO_4)_3$.	*Per cent.* Yt_2O_3.
.7266 grm.	1.4737 grm.	49.304
.7856 "	1.5956 "	49.235

Mean, 49.2695, ± .0233

Cleve's‖ results are published in a joint memoir by Cleve and Hoeglund, and are as follows:

* Ann. Chem. Pharm., 134, 108.
† Arch. des Sci. Phys. et Nat., (2,) 25, 119. 1866.
‡ Ann. Chem. Pharm., 137, 21. 1866.
‖ K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 8.

Yt_2O_3.	$Yt_2(SO_4)_3$.	*Per cent.* Yt_2O_3.
1.4060 grm.	2.8925 grm.	48.608
1.0930 "	2.2515 "	48.545
1.4540 "	2.9895 "	48.637
1.3285 "	2.7320 "	48.627
2.3500 "	4.8330 "	48.624
2.5780 "	5.3055 "	48.591
		Mean, 48.605, ± .0096

This series is unquestionably the best of all. From it, if $SO_3 = 80$, $Yt = 89.485$.

Combining all these data we have the subjoined general mean for the percentage of Yt_2O_3:

Popp	51.208, ± .011
Delafontaine, 1st	49.998, ± .081
" 2d	48.230, ± .055
Bahr and Bunsen	49.2695, ± .0233
Cleve	48.605, ± .0096
General mean	49.637, ± .0069
Rejecting Popp	48.705, ± .0087

From the general mean of all, $Yt = 97.616$. From the mean after excluding Popp's work, $Yt = 89.816, \pm .067$; or, if $O = 16$, $Yt = 90.023$.

YTTERBIUM.

For ytterbium we have one very good set of determinations by Nilson.* The oxide was converted into the sulphate after the usual manner:

Yb_2O_3.	$Yb_2(SO_4)_3$.	*Per cent.* Yb_2O_3.
1.0063 grm.	1.6186 grm.	62.171
1.0139 "	1.6314 "	62.149
.8509 "	1.3690 "	62.155
.7371 "	1.1861 "	62.145
1.0005 "	1.6099 "	62.147
.8090 "	1.3022 "	62.126
1.0059 "	1.6189 "	62.134
		Mean, 62.147, ± .0036

* Compt. Rend., 91, 56. 1880.

Hence Yb = 172.761, ± .038. If O = 16, then Yb = 173.158. If SO_3 = 80, Yb = 173.016. The true number cannot be far from 173.

ERBIUM.

Since the earth which was formerly regarded as the oxide of this metal is now known to be a mixture of two or three different oxides, the older determinations of its molecular weight have little more than historical interest. Neverthe-less the work done by several investigators may properly be cited, since it sheds some light upon certain important problems.

First, Delafontaine's* early investigations may be considered. A sulphate, regarded as erbium sulphate, gave the following data. An oxalate was thrown down from it, which, upon ignition, gave oxide. The percentages in the fourth column refer to the anhydrous sulphate. In the last experiment water was not estimated, and I assume for its water the mean percentage of the four preceding experiments:

Sulphate.	*Er_2O_3.*	*H_2O.*	*Per cent. Er_2O_3.*
.827 grm.	.353 grm.	.177 grm.	54.308
1.0485 "	.4475 "	.226 "	54.407
.803 "	.3415 "	.171 "	54.035
1.232 "	.523 "	.264 "	54.028
1.1505 "	.495 "	------	54.760
		Mean,	54.308, ± .0915

Bahr and Bunsen† give a series of results, representing successive purifications of the earth which was studied. The final result, obtained by the conversion of oxide into sulphate, was as follows:

.7870 grm. oxide gave 1.2765 grm. sulphate. 61.653 per cent. oxide.

Hoeglund,‡ following the method of Bahr and Bunsen, secured these results:

* Ann. Chem. Pharm., 134, 108. 1865.
† Ann. Chem. Pharm., 137, 21. 1866.
‡ K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 6.

Er_2O_3.	$Er_2(SO_4)_3$.	Per cent. Er_2O_3.
1.8760 grm.	3.0360 grm.	61.792
1.7990 "	2.9100 "	61.821
2.8410 "	4.5935 "	61.848
1.2850 "	2.0775 "	61.853
1.1300 "	1.827 "	61.850
.8475 "	1.370 "	61.861
		Mean, 61.8375, ± .0063

Humpidge and Burney* give data as follows:

1.9596 grm. $Er_2(SO_4)_3$ gave	1.2147 grm. Er_2O_3.	61.987 per cent.	
1.9011 "	1.1781 "	61.965 "	
		Mean, 61.976, ± .0074	

Combining all four series we get the subjoined general mean for the percentage of oxide in sulphate. Bahr and Bunsen's single experiment is given the probable error of one experiment in Hoeglund's series:

Delafontaine	54.308,	± .0915
Bahr and Bunsen	61.653,	± .0178
Hoeglund	61.8375,	± .0063
Humpidge and Burney	61.976,	± .0074
General mean	61.860,	± .0046
Rejecting the first	61.880,	± .0046

From the mean of all, Er = 170.379, ± .082; or, if O = 16, Er = 170.770. From Bahr and Bunsen's determination, Er = 168.683; and from Humpidge and Burney's highest, Er = 171.428.

The foregoing data were all published before the composite nature of the supposed erbia was fully recognized. It will be seen, however, that three sets of results were fairly comparable, while Delafontaine evidently studied an earth widely different from that investigated by the others. Since the discovery of ytterbium, some light has been thrown on the matter. The old erbia is a mixture of at least three earths, to one of which, a rose-colored body, the name erbia is now restricted. For the atomic weight of the true erbium

* Journ. Chem. Society, Feb., 1879, p. 116.

Cleve* gives three values, but without data concerning weighings or methods. Doubtless the oxide was converted into sulphate, and the calculations were made with $SO_3 = 80$:

166.00
166.21
166.25

Mean, 166.153

With $SO_3 = 79.874$, this becomes 165.891, and if only O = 16, 166.273. These figures are undoubtedly the nearest yet reached to the true value. According to Thalén,† who reasons from spectroscopic evidence, the erbium of Hoeglund was largely ytterbium.

TERBIUM, SAMARIUM, PHILIPPIUM, DECIPIUM, THULIUM, HOLMIUM, AND SORET'S EARTH X.

Concerning these substances, real or alleged, the data are exceedingly vague. For phillippium Delafontaine‡ gives an atomic weight approximating to 123 or 125, and in the same memoir decipium is put at 171. It seems probable that philippium may be identical with Cleve's holmium and the metal of Soret's earth X, while decipium comes near Cleve's thulium, for which the discoverer gives a value of about 170.7.‖ If decipium and thulium are identical, or if either proves to be erbium or ytterbium contaminated with the other, then we shall have a triad of metals with atomic weights ranging from Er = 166 to Yb = 173, strikingly parallel with lanthanum, cerium, and didymium. If we take the natural arrangement of the elements as tabulated after Mendelejeff's plan, somewhat modified in Roscoe and Schorlemmer's "Treatise on Chemistry,§ we find that such a triad should exist, and, furthermore, that another similar

* Compt. Rend., 91, 382.
† Poggend. Beiblätter, 5, 122. 1881.
‡ Arch. des Sci. Phys. et Nat., Mars, 1880.
‖ Compt. Rend., 91. 329. 1880.
§ Vol. 2, Part 2, p. 507.

group ought to lie between indium and tin. The latter triad should have atomic weights ranging from 114 to 117; and here possibly, or else forming a triad with yttrium, the other metals of this group may lie.

COLUMBIUM.*

The atomic weight of this metal has been determined by Rose, Hermann, Blomstrand, and Marignac. Rose† analyzed a compound which he supposed to be chloride, but which, according to Rammelsberg,‡ must have been nearly pure oxychloride. If it was chloride, then the widely varying results give approximately Cb = 122; if it was oxychloride, the value becomes nearly 94. If it was chloride, it was doubtless contaminated with tantalum compounds.

Hermann's|| results seem to have no present value, and as for Blomstrand's,§ I am not able to get at a copy of his original memoir. The results of the latter chemist are thus summed up in Becker's "Digest." Three chlorine estimations in the pentachloride give, in mean, Cb = 96.67. Eleven weighings of columbic acid from the same compound make Cb = 96.16. Other experiments on sodium columbate lead Blomstrand to regard 95 as the most probable value.

Marignac¶ made about twenty analyses of the potassium fluoxycolumbate, $CbOF_3.2KF.H_2O$. 100 parts of this salt give the following percentages:

Cb_2O_5	Extremes	44.15	to 44.60	Mean, 44.36
K_2SO_4	"	57.60	" 58.05	
H_2O	"	5.75	" 5.98	
F	"	30.62	" 32.22	

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* This name has priority over the more generally accepted "niobium," and therefore deserves preference.

† Poggend. Annal., 104, 439. 1858.

‡ Poggend. Annal., 136, 353. 1869.

|| Journ. für Prakt. Chem., 68, 73. 1856.

§ Acta Univ. Lund, 1864.

¶ Archives des Sci. Phys. et Nat., (2,) 23, 258. 1865.

From the mean percentage of Cb_2O_5, Cb = 93.217. If O = 16, this becomes 93.431.

From the mean between the extremes given for K_2SO_4, Cb = 93.812. If O = 16, this becomes 94.027.

As Deville and Troost's* results for the vapor density of the chloride and oxychloride agree fairly well with Cb = 94, we may adopt this value as approximately correct.

TANTALUM.

The results obtained for the atomic weight of this metal by Berzelius,† Rose,‡ and Hermann ‖ may be fairly left out of account as valueless. These chemists could not have worked with pure preparations, and their data are sufficiently summed up in Becker's "Digest."

Marignac § made four analyses of a pure potassium fluotantalate, and four more experiments upon the ammonium salt. The potassium compound, K_2TaF_7 was treated with sulphuric acid, and the mixture was then evaporated to dryness. The potassium sulphate was then dissolved out by water, while the residue was ignited and weighed as Ta_2O_5. 100 parts of the salt gave the following quantities of Ta_2O_5 and K_2SO_4:

Ta_2O_5.	K_2SO_4.
56.50	44.37
56.75	44.35
56.55	44.22
56.56	44.24
Mean, 56.59, ± .037	Mean, 44.295, ± .026

* Comptes Rend., 56, 891. 1863.
† Poggend. Annal., 4, 14. 1825. Lehrbuch, 3, 1209.
‡ Poggend. Annal., 99, 80. 1856.
‖ Journ. für Prakt. Chem., 70, 193. 1857.
§ Archives des Sci. Phys. et Nat., 26, 89, serie 2. 1866.

From these figures, 100 parts of K_2SO_4 correspond to the subjoined quantities of Ta_2O_5:

127.338
127.960
128.178
127.848

Mean, 127.831, ± .120

The ammonium salt, $(NH_4)_2TaF_7$, ignited with sulphuric acid, gave these percentages of Ta_2O_5. The figures are corrected for a trace of K_2SO_4 which was always present:

63.08
63.24
63.27
63.42

Mean, 63.25, ± .047

Hence we have four values for Ta:

From potassium salt, per cent. Ta_2O_5	Ta	=	183.033, ± .343
" " " K_2SO_4	"	=	181.619, ± .242
" " $K_2SO_4 : Ta_2O_5$	"	=	182.361, ± .411
" ammonium salt, per cent. Ta_2O_5	"	=	182.149, ± .456
General mean	"	=	182.144, ± .166

Or, if O = 16, Ta = 182.562.

If we assume K = 39, O = 16, F = 19, S = 32, and N = 14; the percentage of K_2SO_4 from K_2TaF_7 gives Ta = 181.912; and the analyses of the ammonium salt make Ta = 182.020. Evidently, 182 is not far from the true value.

PLATINUM.

For this metal we have to consider only experiments by Berzelius, by Andrews, and by Seubert. In an early paper Berzelius* reduced platinous chloride, and found it to contain 73.3 per cent. of platinum. Hence, Pt = 194.204, a

* Poggend. Annal., 8, 177. 1826.

value very near that obtained most recently by Seubert. In his later investigations, Berzelius * studied the potassium chloroplatinate, K_2PtCl_6. 6.981 parts of this salt, ignited in hydrogen, lost 2.024 of chlorine. The residue consisted of 2.822 platinum, and 2.135 potassium chloride. From these data we may calculate the atomic weight of platinum in four ways:

1st.	From loss of Cl upon ignition	Pt	= 197.722
2d.	" weight of Pt in residue	"	= 196.942
3d.	" " KCl "	"	= 196.215
4th.	" ratio between KCl and Pt	"	= 196.652

The last of these values is undoubtedly the most reliable, since it involves no errors due to the possible presence of moisture in the salt analyzed. If O = 16, the value becomes Pt = 197.104.

The work done by Andrews † is even less satisfactory than the foregoing, for the reason that its full details seem never to have been published. Andrews dried potassium chloroplatinate at 105°, and then decomposed it by means of zinc and water. The excess of zinc having been dissolved by treatment with acetic and nitric acids, the platinum was collected upon a filter and weighed, while the chlorine in the filtrate was estimated by Pelouze's method. Three determinations gave as follows for the atomic weight of platinum:

197.86
197.68
198.12

Mean, 197.887

If we assume that these values were calculated with K = 39 and Cl = 35.5, the mean, corrected by our later figures for these elements, becomes Pt = 197.382. If O = 16, this becomes Pt = 197.836. Unfortunately, Andrews does not, in his brief note upon the subject, indicate the manner by which his calculations were made.

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* Poggend. Annal., 13, 468. 1828.

† British Association Report, 1852. Chem. Gazette, 10, 380.

Latest of all we have to consider the experiments of Seubert.* This chemist prepared very pure chloroplatinates of ammonium and potassium, and from their composition deduced the atomic weight of the metal under consideration. The ammonium salt, $(NH_4)_2PtCl_6$ was analyzed by heating in a stream of hydrogen, expelling the excess of that gas by a current of carbon dioxide, and weighing the residual metal. In three experiments the hydrochloric acid formed during such a reduction was collected in an absorption apparatus, and estimated by precipitation as silver chloride. Three series of results are given for the percentage of platinum in this salt, together with another single result which may be considered alone. Here are the figures :

Series I.	*Series II.*	*Series III.*
43.957	43.871	43.990
43.948	43.876	43.986
43.960	43.872	44.001
43.946	43.881	44.020
43.963	43.875	43.994
43.961	43.879	43.996
		44.004
Mean, 43.956, ± .002	Mean, 43.876, ± .001	44.026
		43.998
		Mean, 44.001, ± .003

These series represent three preparations. The additional single experiment above referred to was made with material belonging to series II, but recrystallized from water. This salt gave 43.955 per cent. of platinum, a figure to which we may assign the probable error of one experiment in the first series. Combining, we get the subjoined general mean percentage of Pt in $(NH_4)_2PtCl_6$:

Series I	43.956, ± .002
" II	43.876, ± .001
" III	44.001, ± .003
Extra experiment	43.955, ± .004
General mean	43.907, ± .0009

* Ber. der Deutsch. Chem. Gesell., 14, 865. 1881.

Hence Pt = 194.314, ± .078. If N = 14, and Cl = 35.5, then Pt = 194.906. Calculating with Stas' values for N and Cl, Seubert gets from the four results combined above, the following figures for Pt, respectively: 194.685, 194.039, 195.034, 194.665.

For the chlorine estimations in the ammonium salt the subjoined weighings are given:

Salt.	*Pt.*	*AgCl.*
2.7054 grm.	1.1871 grm.	5.2226 grm.
2.2748 "	.9958 "	4.3758 "
3.0822 "	1.3561 "	5.9496 "

Hence 100 parts of AgCl correspond to the following quantities of salt:

51.802
51.986
51.805
Mean, 51.864, ± .041

Hence, calculating directly from the ratio between 6AgCl and $(NH_4)_2PtCl_6$, Pt = 196.871, ± .363.

Seubert himself reckons the percentage of chlorine from the weight of silver chloride, and then calculates the ratio between Cl_6 and Pt. He thus finds, with Stas' value for Cl, Pt = 195.330.

The potassium salt, K_2PtCl_6, was also analyzed by ignition in hydrogen, treatment with water, and weighing both the platinum and the potassium chloride. These percentages were found:

Pt.	*KCl.*
40.119	30.706
40.120	30.728
40.076	30.698
40.070	30.666
40.107	30.700
40.120	30.627
40.114	30.710
40.130	30.621
Mean 40.107, ± .005	Mean, 30.682, ± .009

From the first column.......Pt = 194.370, ± .068
" second " .... " = 194.645, ± .213

If K = 39, and Cl = 35.5, the first column gives Pt = 194.933. Seubert, from the percentage of platinum, gets Pt = 194.392; and from the ratio 2KCl : Pt he finds Pt = 194.494.

As with the ammonium salt, three experiments were made upon the potassium compound to determine the amount of chlorine lost upon reduction in hydrogen. I cite the weighings, and add in a fourth column the quantity of K_2PtCl_6 proportional to 100 parts of AgCl. This AgCl represents but *four* atoms of the chlorine:

Salt.	*Pt.*	*AgCl.*	*Ratio.*
6.7771 grm.	2.7158 grm.	7.9725 grm.	85.006
3.5834 "	1.4372 "	4.2270 "	84.774
4.4139 "	1.7713 "	5.2144 "	84.648
			Mean, 84.809, ± .071

Hence Pt = 195.002, ± .415. If K = 39, Ag = 108, and Cl = 35.5, then Pt = 194.955. Seubert, calculating the percentage of chlorine and thence the ratio Cl_4 : Pt, gets Pt = 194.631.

Combining all the values we have the following result for the atomic weight of platinum:

1.	From per cent. Pt in $(NH_4)_2PtCl_6$	Pt	= 194.314, ± .078
2.	" $6AgCl : (NH_4)_2PtCl_6$ ratio	"	= 196.871, ± .363
3.	" per cent. Pt in K_2PtCl_6	"	= 194.370, ± .068
4.	" " KCl "	"	= 194.645, ± .213
5.	" $4AgCl : K_2PtCl_6$ ratio	"	= 195.002, ± .415
	General mean	"	= 194.415, ± .040

Or, if O = 16, Pt = 194.867.

Seubert, taking the arithmetical mean of his eight values, gets Pt = 194.620. He regards, however, those results as best which are dependent upon the percentage of platinum in the ammonium salt, and upon the complete analysis of the potassium compound. These give him a mean of Pt = 194.461, which, if corrected by reduction to a vacuum standard, becomes Pt = 194.34.

In will be noticed that three of the ratios, calculated with

$K = 39$, $N = 14$, $Ag = 108$, and $Cl = 35.5$, give nearly $Pt = 195$, namely:

194.906
194.933
194.955

The general mean of all, if $O = 16$, gives $Pt = 194.867$. Hence, for all practical calculations, the value 195 may be safely employed.

OSMIUM.

The atomic weight of this metal has been determined by Berzelius and by Fremy.

Berzelius* analyzed potassium osmichloride, igniting it in hydrogen like the corresponding platinum salt. 1.3165 grammes lost .3805 of chlorine, and the residue consisted of .401 grm. of potassium chloride, with .535 grm. of osmium. Calculating only from the ratio between the Os and the KCl, we have, $Os = 198.494$; or, if $O = 16$, $Os = 198.951$.

Fremy's determination† is based upon the composition of osmium tetroxide. No details as to weighings or methods are given; barely the final result is stated. This, if $O = 15.9633$, is $Os = 199.190$. If $O = 16$, $Os = 199.648$.

Berzelius' work is evidently entitled to preference, although neither determination is in any sense equal to the present requirements of chemical science. The values given are doubtless several units too high.

IRIDIUM.

The only early determination of the atomic weight of iridium was made by Berzelius,‡ who analyzed potassium iridichloride by the same method employed with the platinum and the osmium salts. The result found from a single

* Poggend. Annal., 13, 530. 1828.
† Compt. Rend., 19, 468. Journ. für Prakt. Chem., 33, 410. 1844.
‡ Poggend. Annal., 13, 435. 1828.

analysis was not far from Ir = 196.7. This is now known to be too high. I have not, therefore, thought it worth while to recalculate Berzelius' figures, but give his estimation as it is stated in Roscoe and Schorlemmer's "Treatise on Chemistry."

In 1878 the matter was taken up by Seubert,* who had at his disposal 150 grammes of pure iridium. From this he prepared the iridichlorides of ammonium and potassium, $(NH_4)_2IrCl_6$ and K_2IrCl_6, which salts were made the basis of his determinations. The potassium salt was dried by gentle heating in a stream of dry chlorine.

Upon ignition of the ammonium salt in hydrogen, metallic iridium was left behind in white coherent laminæ. The percentages of metal found in seven estimations were as follows:

43.742
43.725
43.745
43.739
43.726
43.739
43.705
Mean, 43.732, ± .0035

The potassium salt was also analyzed by decomposition in hydrogen with special precautions. In the residue the iridium and the potassium chloride were separated after the usual method, and both were estimated. Eight analyses gave the following results, expressed in percentages:

	Ir.	*2KCl.*	*Cl_4.*
	39.881	30.829	29.290
	39.890	30.842	29.277
	39.868	30.813	29.300
	39.876	30.835	29.289
	39.877	30.825	29.287
	39.879	30.811	29.310
	39.882	30.814	29.285
	39.883	30.792	29.288
Mean,	39.880, ± .0015	30.820, ± .0037	29.291, ± .0024

* Ber. d. Deutsch. Chem. Gesell., 11, 1767.

From these data several values for the atomic weight of iridium may be calculated:

From per cent. Ir in $(NH_4)_2IrCl_6$	Ir =	192.951, ± .064
" " K_2IrCl_6	" =	192.536, ± .060
" KCl in "	" =	192.474, ± .111
" Cl_4 in "	" =	192.757, ± .148
General mean	" =	192.702, ± .039

If O = 16, this becomes Ir = 193.145.

In the potassium salt, instead of calculating from the percentages directly, we may reckon upon the ratios between Ir and Cl_4, and between Ir and 2KCl:

From Ir : Cl_4 ratio	Ir =	192.626, ± .081
" Ir : 2KCl ratio	" =	192.514, ± .044
General mean	" =	192.539, ± .039

Or, if O = 16, Ir = 192.982.

Again, we may combine this mean with the value derived from the ammonium iridichloride, and so estimate the relative importance of the latter:

From K_2IrCl_6	Ir =	192.539, ± .039
" $(NH_4)_2IrCl_6$	" =	192.951, ± .064
General mean	" =	192.651, ± .033

If O = 16, this becomes Ir = 193.094.

We may assume, then, from all the facts before us, that if O = 16, the atomic weight of iridium varies from the even number 193 only within the limits of experimental error.

PALLADIUM.

The atomic weight of palladium has been studied by Berzelius and by Quintus Icilius. In an early paper Berzelius* found that 100 parts of the metal united with 28.15 of sulphur. Hence Pd = 113.63, a result which is unquestionably far too high.

* Poggend. Annal., 8. 177. 1826.

In a later paper* Berzelius published two analyses of potassium palladiochloride, K_2PdCl_4. The salt was decomposed by ignition in hydrogen, as was the case with the double chlorides of potassium with platinum, osmium, and iridium. Reducing his results to percentages, we get the following composition for the substance in question:

	Pd.	*2KCl.*	*Cl_2.*
	32.726	46.044	21.229
	32.655	45.741	21.604
Mean,	32.690	45.892	21.416

From these percentages, calculating directly, very discordant results are obtained:

From percentage of metal ---------- Pd = 106.612
" " KCl ------------ " = 104.674
" " Cl_2, (loss) ------ " = 110.796

Obviously, the only way to get satisfactory figures is to calculate from the ratio between the Pd and 2KCl. Doing this, we get, Pd = 105.737; or, if O = 16, Pd = 105.981.

This last value varies so slightly from the even number 106 that the latter may be safely used for all purposes of chemical calculation.

The determination made by Quintus Icilius* need be given only for the sake of completeness. He ignited potassium palladichloride in hydrogen, and found the following amounts of residue. His weights are here recalculated into percentages:

64.708
64.965
64.781

Mean, 64.818

From this mean, Pd = 111.879. Upon looking at the values deduced from Berzelius' figures, it will be seen that

* Poggend. Annal., 13, 454. 1828.

† "Die Atomgewichte vom Pd, K, Cl, Ag, C, und H, nach der Methode der kleinsten Quadrate berechnet." Inaug. Diss. Göttingen, 1847. Contains no other original analyses.

the highest, 110.796, is calculated from the chlorine lost upon igniting the palladiochloride. The same kind of error which vitiates that result probably affects also these data drawn from the palladiochloride.

RHODIUM.

Berzelius* determined the atomic weight of this metal by the analysis of sodium and potassium rhodiochlorides, Na_3RhCl_6, and K_2RhCl_5. The latter salt was dried by heating in chlorine. The compounds were analyzed by reduction in hydrogen, after the usual manner. Reduced to percentages the analyses come out as follows:

In Na_3RhCl_6.

Rh.	*3NaCl.*	*Cl_3.*
26.959	45.853	27.189
27.229	45.301	27.470
		27.616
Mean, 27.094	45.577	27.425

In K_2RhCl_5.

Rh.	*2KCl.*	*Cl_3.*
28.989	41.450	29.561

From the analyses of the sodium salt we get the following values for Rh:

From per cent. of metal	Rh = 104.507
" " NaCl	" = 102.980
" " Cl_3	" = 105.696
" ratio between Cl_3 and Rh	" = 104.829
" " NaCl "	" = 104.093

These are discordant figures, and indicate some doubt as to purity of material. The last value is fairly good, however, and is confirmed by results from the potassium compound:

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* Poggend. Annal., 13, 435. 1828.

From per cent. of metal	Rh	=	104.054
" " KCl	"	=	104.046
" " Cl_3	"	=	104.065
" Rh : Cl_3 ratio	"	=	104.057
" Rh : KCl ratio	"	=	104.051
Mean	"	=	104.055

If O = 16, this becomes Rh = 104.285.

RUTHENIUM.

The atomic weight of this metal has been determined only by Claus.* Although he employed several methods, the only results worthy of present notice come from the analysis of potassium rutheniochloride, K_2RuCl_5. The salt was dried by heating to 200° in chlorine gas, but even then retained a trace of water. The percentage results of analysis are as follows:

	Ru.	*2KCl.*	*Cl_3.*
	28.96	40.80	30.24
	28.48	41.39	30.22
	28.91	41.08	30.04
Mean,	28.78	41.09	30.17

Reckoning directly from the percentages we get the following discordant values for Ru:

From percentage of metal	Ru	=	103.016
" " KCl	"	=	107.190
" " Cl_3	"	=	96.854

Obviously, the best result is to be obtained from the ratio between Ru and 2KCl. This gives Ru = 104.217; or, if O = 16, Ru = 104.457. But little weight can be attached to this determination.

* Journ. für Prakt. Chem., 34, 435. 1845.

APPENDIX.

ON DUMAS' CORRECTION AND PROUT'S HYPOTHESIS.

In the year 1815 Prout put forth his famous hypothesis that the atomic weights of all the elements were multiples of that of hydrogen. His views were adopted by many chemists, but opposed by others; among them Berzelius and Turner; and down to the present day "Prout's Law" has been the subject of earnest controversy. Of course the fact was early recognized that in its original form the hypothesis could not stand, and accordingly it was modified by Dumas in such manner that half and quarter multiples of the atomic weight of hydrogen were considered as well as the whole numbers.

But of late years Prout's hypothesis, even with its elastic modification, has been in disfavor. Only a few chemists still clung to it as the representative of a veritable law. The researches of Stas were especially directed towards ascertaining its truth or falsity; and his results, as well as those obtained by Marignac, were such as to lead most chemists to the belief that it had been forever overthrown. The atomic weights determined by Stas agreed neither with whole, half, nor quarter multiples of that of hydrogen, and the variations seemed to be wholly outside the range of recognizable experimental errors.

In 1878, however, a probable source of error in some of Stas' researches was pointed out by Dumas.* Many of Stas' ratios had involved the use of pure metallic silver, which had been fused under a cover of borax containing a little

* Ann. Chim. Phys., (5s.,) 14, 289.

nitre. Such silver Dumas heated to redness in a Sprengel vacuum, and found that it gave up weighable quantities of oxygen, which had been absorbed by the metal when in the melted state. In one experiment a kilogramme of silver gave 82 milligrammes of occluded gas, and in three other cases 226, 140, and 249 milligrammes respectively were found. In other words, the silver which had been considered pure by Stas and others, was really not pure, and a correction became necessary in nearly all series of atomic weight determinations.

The amount of this correction, which I think may hereafter be appropriately designated as "Dumas' correction," will naturally vary in different cases, and in no particular case can we tell, without actual examination of the silver employed, exactly how great it should be. We may, however, assume that all the metallic silver heretofore used in establishing atomic weight ratios was subject to it; and, reckoning from the largest error indicated in the experiments of Dumas, namely, 249 milligrammes of oxygen in the kilogramme of metal, we may ascertain its tendency with reference to Prout's law.

In the chapter upon the atomic weights of silver, chlorine, bromine, iodine, potassium, sodium, and sulphur, twenty ratios are given, of which nine are subject to Dumas' correction. Applying it as suggested above, we get the following results. The values previously found and given in the chapter just quoted, we may designate as uncorrected. For convenience in future reference I assume that O = 16:

	Uncorrected.	*Corrected.*	*Difference.*
Silver	107.923	107.896	— .027
Chlorine	35.451	35.478	+ .027
Bromine	79.951	79.978	+ .027
Iodine	126.848	126.875	+ .027
Potassium	39.109	39.083	— .026
Sodium	23.051	23.024	— .027
Sulphur	32.058	32.058	------

The result of the correction, it will be seen, is generally favorable to Prout's hypothesis. Of the seven elements

under consideration, one has its atomic weight unaffected, one is rendered less in accord with the hypothesis, and five approximate more closely than before to even multiples or multiples half of hydrogen.

In the later chapters of this work the effect of Dumas' correction is generally less striking. One general statement, however, may be made concerning it. Whenever the atomic weight of a metal is calculated from the ratio between its haloid salts and metallic silver, the total effect of Dumas' correction, including the above corrections for the halogens themselves, will be to *lower* the final result. This point will be further considered presently. Only chlorine, bromine, and iodine have their atomic weights raised by the correction.

In view of Dumas' correction the question naturally arises as to how far other metals, used in atomic weight researches, may occlude gaseous impurities. For example, when the atomic weight of oxygen is fixed by the synthesis of water over copper oxide, may not the copper occlude appreciable quantities of the hydrogen in which it cools? If it does, then the apparent weight of metallic copper would be too high, and the atomic weight of oxygen would come out too low. Such an error might possibly account for the difference between 16 and 15.9633 in the atomic weight of oxygen, and it would also increase the atomic weight of copper as determined by the same process. At all events, every metal of which the atomic weight has been determined by the reduction of its compounds in hydrogen, ought to be scrupulously investigated with reference to the possible occlusion of gaseous impurities. With all of these metals the effect of such impurities would be to render the apparent atomic weights decidedly too high.

Although every series of atomic weight determinations must be considered by itself, and weighed on its own merits, it may not be out of place for me just here to point out two general sources of error in addition to the one we have been considering. First, every value after oxygen, with one or two partial exceptions, involves whatever error may attach

to the atomic weight of oxygen. If the latter be 16, instead of 15.9633, this error in some instances becomes multiplied to a large fraction of a unit, as the subjoined example will show.

If O = 16, the atomic weight of uranium		= 239.030
If O = 15.9633,	" "	= 238.482
Difference		0.548

Other similar errors are repeated continually. The value assigned to any element is necessarily affected by whatever errors may attach to the atomic weights of those other elements through whose medium it is compared with the standard, hydrogen. Thus, the atomic weight of carbon depends upon that of oxygen; calcium depends upon both carbon and oxygen; and fluorine, as determined from calcium fluoride, involves the foregoing elements, together with sulphur, silver, and chlorine. Since, however, some atomic weights are affected by plus errors and others by minus errors, there is a fortunate tendency to compensation of errors in cases like that of fluorine, and, in reality, better results are obtained than considerations such as these would lead us to look for.

Another general source of error is to be found in the fact that some of the weighings involved in our discussions had been reduced to absolute standards, while others were merely uncorrected weighings in air. The errors thus introduced into the work are doubtless small, but still they ought not to be absolutely ignored.

Now, having considered the larger classes of errors, we may properly pass on to a comparison of our atomic weights with reference to Prout's hypothesis. In order to facilitate work, I have tabulated the figures in two columns, one giving atomic weights referred to hydrogen as unity, the other based upon the standard of oxygen as exactly sixteen. Such imperfectly known elements as decipium, philippium, samarium, terbium, and thulium are not included.

TABLE OF ATOMIC WEIGHTS.

	H = 1.	O = 16.	Remarks.
Aluminum	27.009, ± .003	27.075	
Antimony	119.955, ± .036	120.231	Cooke's and Schneider's data.
Arsenic	74.918, ± .016	75.090	
Barium	136.763, ± .031	137.007	
Bismuth	207.523, ± .082	208.001	From Schneider's data.
Boron	10.941, ± .023	10.966	
Bromine	79.768, ± .019	79.951	
Cadmium	111.835, ± .024	112.092	
Cæsium	132.583, ± .024	132.918	
Calcium	39.990, ± .010	40.082	
Carbon	11.9736, ± .0028	12.0011	
Cerium	140.424, ± .017	140.747	Buehrig's data give 141.523. (O = 16.)
Chlorine	35.370, ± .014	35.451	
Chromium	52.009, ± .025	52.129	From Siewert's data.
Cobalt	58.887, ± .008	59.023	
Columbium	93.812	94.027	From one ratio only.
Copper	63.173, ± .011	63.318	
Didymium	144.573, ± .031	144.906	Cleve's data give 147.021. (SO_3 = 80.)
Erbium	165.891	166.273	From Cleve's data only.
Fluorine	18.984, ± .0065	19.027	
Gallium	68.854	68.963	Imperfectly determined.
Glucinum	9.085, ± .0055	9.106	Nilson and Pettersson's data.
Gold	196.155, ± .095	196.606	
Hydrogen	1.0000	1.0023	
Indium	113.398, ± .047	113.659	
Iodine	126.557, ± .022	126.848	
Iridium	192.651, ± .033	193.094	Seubert's data.
Iron	55.913, ± .012	56.042	
Lanthanum	138.526, ± .030	138.844	
Lead	206.471, ± .021	206.946	
Lithium	7.0073, ± .007	7.0235	
Magnesium	23.959, ± .005	24.014	Marchand and Scheerer's data.
Manganese	53.906, ± .012	54.029	Schneider and Rawack's data.
Mercury	199.712, ± .042	200.171	
Molybdenum	95.527, ± .051	95.747	
Nickel	57.928, ± .022	58.062	Schneider, Sommaruga, and Lee.
Nitrogen	14.0210, ± .0035	14.029	
Osmium	198.494	198.951	Very doubtful.
Oxygen	15.9633, ± .0035	16.000	
Palladium	105.737	105.981	Badly determined.
Phosphorus	30.958, ± .007	31.029	
Platinum	194.415, ± .049	194.867	Seubert's data.
Potassium	39.019, ± .012	39.109	
Rhodium	104.055	104.285	Badly determined.
Rubidium	85.251, ± .018	85.529	
Ruthenium	104.217	104.457	Badly determined.
Scandium	43.980, ± .015	44.081	
Selenium	78.797, ± .011	78.978	

TABLE OF ATOMIC WEIGHTS—CONTINUED.

	H = 1.		O = 16.	Remarks.
Silicon	28.195,	± .066	28.260	Very badly determined.
Silver	107.675,	± .0096	107.923	
Sodium	22.998,	± .011	23.051	
Strontium	87.374,	± .032	87.575	
Sulphur	31.984,	± .012	32.058	
Tantalum	182.144,	± .166	182.562	
Tellurium	127.960,	± .034	128.254	Imperfectly determined.
Thallium	203.715,	± .0365	204.183	Crookes' data.
Thorium	233.414,	± .073	233.951	
Tin	117.698,	± .040	117.968	
Titanium	49.846,	± .064	49.961	Imperfectly determined.
Tungsten	183.610,	± .032	184.032	
Uranium	238.482,	± .082	239.030	
Vanadium	51.256,	± .024	51.373	
Ytterbium	172.761,	± .038	173.158	If $SO_3 = 80$, Yb = 173.016.
Yttrium	89.816,	± .067	90.023	Doubtful.
Zinc	64.9045,	± .019	65.054	Axel Erdmann's data.
Zirconium	89.367,	± .037	89.573	Doubtful.

At the close of his admirable paper on the atomic weight of aluminum Mallet makes substantially the following argument in favor of Prout's hypothesis. Citing the atomic weights of eighteen elements which he considers well determined, he shows that ten of them have values falling within one-tenth of a unit of whole numbers. Now, what is the mathematical probability that this close approximation to conformity with Prout's law, in ten cases out of eighteen, is purely accidental, as those chemists who reject the hypothesis seem to hold? Working this problem out, Mallet finds the probability in favor of mere coincidence to be in the ratio of 1 : 1097.8, and hence he concludes that Prout's views are still worthy of respectful consideration.

Applying Mallet's reasoning to the table of atomic weights now before us, we find that in the first column, when H = 1, twenty-five elements out of sixty-six have values falling within the limits of one-tenth of a unit variation from whole numbers. But many of the figures which fall without this limit involve the variation of oxygen multiplied many times over. We must therefore study the second column, which assumes that the atomic weight of oxygen is exactly six-

teen. Here we have forty elements falling within the limit of variation assigned by Mallet, and twenty-six falling without. The variations we may properly study in some detail.

Taking first the elements whose atomic weights vary from even multiples of unity by less than a tenth of a unit, we have to consider the following: aluminum, arsenic, barium, bismuth, boron, bromine, cadmium, cæsium, calcium, carbon, cobalt, columbium, didymium, fluorine, gallium, hydrogen, iridium, iron, lead, lithium, magnesium, manganese, nickel, nitrogen, osmium, oxygen, palladium, phosphorus, scandium, selenium, silver, sodium, sulphur, thorium, tin, titanium, tungsten, uranium, yttrium, and zinc. Of these, aluminum, arsenic, barium, bismuth, cadmium, calcium, carbon, cobalt, columbium, fluorine, hydrogen, iridium, iron, lithium, magnesium, manganese, nickel, nitrogen, phosphorus, scandium, sodium, sulphur, tungsten, uranium, yttrium, and zinc have plus variations, while boron, bromine, cæsium, didymium, gallium, lead, osmium, palladium, selenium, silver, thorium, tin, and titanium fall slightly under the units to which they approximate. Oxygen, as the standard of comparison, of course shows here no variation, its possible error having been transferred to hydrogen.

Of the foregoing elements it will be seen that twenty-six have plus variations from whole numbers, while thirteen are minus. Among the latter, boron, gallium, osmium, palladium, thorium, and titanium have been but roughly determined. Bromine, by Dumas' correction, has its variation diminished. In the cases of lead, cæsium, selenium, and tin, the cause of variation, supposing one to exist, remains to be determined. The value for osmium is undoubtedly several units too high, so that its agreement with Prout's law may be considered purely accidental. As for didymium, the figure assigned is the mean of all determinations; whereas Clève's data, calculated with $SO_3 = 80$, make $Di = 147.021$, a variation which, like most of the others, is far within the limits of ordinary experimental error. In the

case of silver it has already been shown that Dumas' correction is unfavorable to it considered in its bearings upon Prout's law. Silver is the only element among those having minus variations which could carry very much weight against the hypothesis.

Among the elements whose variations are plus, columbium, uranium, and yttrium have been poorly determined. Yttrium especially may be considered doubtful. The atomic weights of aluminum, arsenic, barium, cadmium, lithium, phosphorus, and sodium involve Dumas' correction to a greater or less extent, and will be lowered by its application, that is, brought nearer to whole numbers. For aluminum, certain other causes for variation were pointed out in the chapter upon that metal; and it may be noted that the direct ratio between it and hydrogen gives Al = 27.998, $\pm$ .007. Here the variation is less than the probable error. For calcium, and consequently for fluorine also, sources of plus error were indicated in the discussion of their respective atomic weights, and reiteration here is unnecessary. Cobalt, iridium, iron, nickel, and tungsten all involve such errors as may arise from the possible occlusion of hydrogen by the metals after reduction from their compounds. For scandium, the atomic weight, calculated with $SO_3 = 80$, becomes 44.032, a variation much within the limits of experimental error. For carbon and bismuth the variations are insignificant. In short, in the majority of instances the errors may be diminished by corrections which are in all probability needed, and which can be easily pointed out. The more carefully we scrutinize the data the more probable Prout's hypothesis appears.

Among the twenty-six elements whose atomic weights are removed by more than a tenth of a unit from whole numbers, chlorine, rubidium, and strontium have values nearly half multiples of that of hydrogen, and in each case Dumas' correction will make the approximation still closer. Erbium, gold, indium, lanthanum, rhodium, ruthenium, silicon, and zirconium may be dismissed from consideration as too imperfectly determined to carry much weight in the present

discussion. For chromium, copper, molybdenum, and vanadium I have no criticisms to offer; but the remaining elements may be considered individually.

The value assigned to antimony, 120.231, is the general mean of Cooke's and Schneider's work upon the bromide, iodide, and sulphide. If Ag = 108, Br = 80, and I = 127, Cooke's data for the bromide and iodide give the following values for Sb, all of which fall within a tenth of a unit of the whole number 120:

Early bromide series	Sb = 119.901
Late "	" = 120.009
Iodide series	" = 119.973

In the case of cerium, the value assigned in the table is the general mean of all reputable determinations. But it is subject to doubt on account of the facts observed by Wolf and by Wing, whose ceroso-ceric oxide was white, while that of all other observers was yellowish. Wolf's and Wing's data, calculated with O = 16, give Ce = 138.039. Cerium, then, is not an *established* exception to Prout's law.

Glucinum and ytterbium have their atomic weights calculated from analyses of the sulphates. But if Prout's law is true, SO_3 = 80. Calculated with this figure, we have Gl = 9.096 and Yb = 173.016. Both elements thus fall within reasonable limits of variation from the hypothetical values.

Iodine is one of the most important seeming exceptions. If we assume Ag = 108, and calculate the atomic weight of iodine only from the direct ratio between iodine and silver, we have, with Dumas' correction applied, I = 126.966; that is, it comes within one-tenth of a unit of the whole number 127.

The atomic weight of mercury depends upon analyses of the chloride, oxide, and sulphide. Of these three compounds the purity of the chloride is most easily assured. Calculated from its composition, with Cl = 35.5, Hg = 199.971. With so high an atomic weight small errors are easily multiplied.

For the atomic weight of platinum Seubert's data give five values, ranging both above and below the round number 195. Calculated with integer values for the other elements, three of these figures fall very close to 195, as follows:

From per cent. Pt in $(NH_4)_2PtCl_6$	Pt	= 194.906
" " K_2PtCl_6	"	= 194.933
From chlorine estimation in K_2PtCl_6	"	= 194.955

Potassium is the most serious exception of all. But if O = 16 and Dumas' correction be applied, the general mean from all the available data becomes K = 39.083. That is, potassium falls within the limit of 0.1 variation.

The atomic weight assigned to tantalum is the mean of four values. Two of these, recalculated with integers, come out as follows:

From per cent. K_2SO_4 in K_2TaF_7	Ta	= 181.912
" Ta_2O_5 from $(NH_4)_2TaF_7$	"	= 182.020

For tellurium I need only call attention to the discrepancies between the several sets of determinations made by Wills. A reference to the chapter on tellurium will show that his figures give results ranging from Te = 126.07 to Te = 129.34. The mean value is therefore too much subject to doubt to carry weight as an exception.

As for thallium, the last case to be considered, I have already shown that Crookes' data, recalculated with integer values for N and O, give Tl = 204.008. That is, instead of an exception, we have here an admirable instance in support of Prout's hypothesis.

Enough has been said in this brief resumé to show that none of the seeming exceptions to Prout's law are inexplicable. Some of them, indeed, carefully investigated, support it strongly. In short, admitting half multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors, than that the great number of close agreements should be merely accidental. I began this recalculation of the atomic weights

with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it a very respectful consideration. All chemists must at least admit that the strife over it is not yet ended, and that its opponents cannot thus far claim a perfect victory.

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299		Annual Report of Smithsonian Institution for 1876,	8vo.	488	1877	
300	Keen, W. W.	Toner Lecture V. Continued Fevers,	M. C. XV,	72	1877	.25
301		Check List of Smithsonian Publications to July, 1877,	M. C. XIV,	72	1877	
302	Adams, Wm.	Toner Lecture VI. Subcutaneous Surgery,	M. C. XV.	20	1877	.25
303	Streets, Thos. H.	Natural History of Hawaiian and Fanning Islands and Lower California. Bulletin National Museum, No. 7,	M. C. XIII,	172	1877	
304	Dall, Wm. H.	Index to names applied to Brachiopoda. Bulletin Nat. Mus., No. 8,	M. C. XIII,	88	1877	
305	Jordan, David S.	North Amer. Ichthyology, No. 1. Review of Rafinesque's N. Am. Fishes. Bulletin of Nat. Mus., No. 9,	M. C. XIII,	53	1877	
306	Jordan, David S.	North Amer. Ichthyology, No. 2. Notes on Cottidae, &c. Bull. Nat. Mus., No. 10.	M. C. XIII,	120	1877	
307	Baird, S. F.	Report on Centennial Exhibition of 1876,	R. 1876,	22	1877	

No.	Author.	Title.	Size or Series.	Pages.	Date.	Price.
308	**Jordan, D. S., and Brayton, A. W.**	North Amer. Ichthyology, No. 3 Distribution of Fishes of S. C., Ga., and Tenn. Bulletin Nat Museum, No. 12,	M. C.	237	1878	
309		List of Foreign Correspondents of the Smithsonian Institution to Jan. 1878,	M. C. xv,	120	1878	
310	**Barnard, J. G.**	Internal Structure of the Earth,	S. C. xxiii,	19	1877	.25
311	**Holden, Edw. S.**	Index Catalogue of Books Relating to Nebulæ,	M. C. xiv,	126	1877	.50
312		Smithsonian Miscellaneous Coll. (Bull. N. M., 1-10.)	M. C. xiii,	982	1878	
313	**Eggers, Baron,**	Flora of St. Croix and Virgin Islands. Bull. Nat. Mus., No. 13,	M. C.	136	1879	
314		Smithsonian Miscellaneous Collections.	M. C. xiv,	911	1878	
315		Smithsonian Miscellaneous Collections.	M. C. xv,	880	1878	
316		Circular in Reference to American Archæology,	M. C. xv,	15	1878	free
317	**Elliot, D. G.**	Classification and Synopsis of Trochilidæ,	S. C. xxiii,	289	1879	3.00
318	**Dall, Wm. H.**	Remains of Man from Caves in Aleutian Islands.	S. C. xxii,	44	1878	2.00
319	**Baird, S. F.**	Circular. Inquiries Relative to Crawfish and Crustacea,	M. C. xv,	8	1878	free
320	**Baird, S. F.**	Circular Relating to Collections of Living Reptiles,	M. C. xv,	2	1878	free
321	**Shakespeare, E. O.**	Toner Lecture, VII. Inflammation in Arteries after Ligature, etc.	M. C. xvi,	74	1879	.25
322		Smithsonian Miscellaneous Collections.	M. C. xvi,	950	1880	
323		Annual Report of the Smithsonian Institution for 1877,	8vo.	500	1878	
324		Circular relative to Scientific and Literary Exchanges,	M. C. xvi,	2	1879	free
325		Circular. Business Arrangements of the Smithsonian Institution,	M. C. xvi,	7	1879	free
326	**Goode, G. Brown,**	Catalogue of Collection of Animal Resources and Fisheries of U. S. Bulletin Nat. Museum, No. 14,	M. C.	367	1879	

No.	Author.	Title.	Size or Series.	Pages.	Date.	Price.
327	**Smithson, James,**	Scientific writings of,	M. C. XXI,	166	1879	.75
328	**Rhees, Wm. J.**	Smithsonian Institution. Documents Relative to its Origin and History,	M. C. XVII,	1027	1879	2.50
329	**Rhees, Wm. J.**	Smithsonian Institution. Journals of Board of Regents and Reports of Committees,	M.C.XVIII,	851	1879	2.00
330	**Rhees, Wm. J.**	Smithson and his Bequest,	M. C. XXI,	76	1879	.75
331	**Rau, Charles,**	The Palenque Tablet,	S. C. XXII,	90	1879	2.00
332		Proceedings of the Nat. Museum for 1878. Vol I,	M. C. XIX,	524	1879	1.00
333		Proceedings of the Nat. Museum for 1879. Vol. II,	M. C. XIX,	504	1880	1.00
334	**Elliot, D. G.**	List of Described Species of Humming-Birds,	M. C. XVI,	22	1879	.25
335	**Rhees, Wm. J.**	List of Principal American Libraries, Museums, Societies, etc.,	M. C. XVI,	6	1879	free
336		Smithsonian Miscellaneous Collections,	M. C. XVII,	1034	1880	
337		Smithsonian Miscellaneous Collections,	M.C. XVIII,	851	1880	
338	**Welling, J. C.**	Life and Character of Joseph Henry,	M. C. XXI,	30	1880	
339	**Taylor, Wm. B.**	The Scientific Work of Joseph Henry,	M. C. XXI,	225	1880	
340		Smithsonian Contributions to Knowledge,	S. C. XXII,	544	1880	
341		Annual Report of Smithsonian Institution for 1878,	8vo.	575	1879	
342	**Kumlien, L.**	Contributions to Natural History of Arctic America. Bulletin of the National Museum, No. 15,	M. C.	179	1879	
343	**Henry, Joseph,**	Annual Reports of Sec. of S. I., 1865-77,	R.	548	1880	free
344		Check List of Smithsonian Publications,	M. C. XVI,	16	1879	free
345		Annual Report of Smithsonian Institution for 1879,	8vo.	631	1880	
346		Smithsonian Contributions to Knowledge,	S. C. XXIII,	766	1881	
347		Cloud Charts,		2	1851	free

No.	Author.	Title.	Size or Series.	Pages.	Date.	Price.
348	Baird, S. F.	Fishes of New Jersey Coast,	R. 1854,	40	1855	
349	Waring, G. E.	Toner Lecture VIII. Sanitary Drainage of Washington.	M. C.	26	1880	.25
350		Map of Stars. (For Aurora obs.)	*	1	1856	free
351	Cooper, J. G.	Forests of North America,	R 1858,	36	1859	
352	Whitney, W. D.	Lectures on Linguistics,	R. 1863,	22	1864	free
353	Schott, C. A.	Tables of Rain Fall, (2d edition).	S. C.	269	1881	3.00
354	Delaunay, M.	Essay on Velocity of Light,	R. 1864,	31	1864	free
355	Wetherill, C. M.	Ozone and Antozone,	R. 1864,	12	1864	
356		Memorial of Joseph Henry,	M. C. XXI,	532	1880	free
357	Wood, H. C.	Researches on Fever,	S. C. XXIII,	263	1878	2.50
358	Becker, G. J.	Atomic Weights. Constants of Nature. Part IV,	M. C.	152	1880	1.00
359		Planisphere of the Heavens,	*	1	1864	free
360	Desor, E.	Palafittes, or Lacustrian Constructions,	R. 1865,	53	1865	
361	Baegert, J.	Aborigines of California,	R. 1863–4,	41	1865	
362	Rau, Charles,	Artificial Shell Deposits in New Jersey,	R. 1864,	6	1865	
363	Lewis, James,	Instructions for collecting Land and Fresh Water Shells,	R. 1866,	8	1860	free
364	Lilljeborg, W.	Classification of Birds,	R 1865,	16	1866	free
365	Ross, Hardisty, Jones, Gibbs,	Tinneh or Chepewyan Indians,	R. 1866,	25	1836	
366	Edwards, A. M.	Directions for collecting Diatomacea,	*	7	1867	free
367	Rothrock, J. T.	Flora of Alaska,	R. 1867,	33	1867	free
368	Rau, Charles,	Indian Pottery,	R. 1866,	11	1867	
369	Abbe, C.	Dorpat and Poulkova,	R. 1867,	23	1867	
370	Rau, Charles,	Flint Implements in Illinois,	R. 1868,	9	1868	
371	Newton, H. A.	Metric Tables,	R. 1865,	23	1868	free
372	Rau, Charles,	Drilling in Stone without Metal,	R. 1868,	11	1869	
373		Meteorological Stations and Observers,	R. 1868,	42	1869	free
374	Schott, C. A.	Rain Charts for Summer, Winter, and Year,	S. C. XVIII,	3	1870	free

No.	Author.	Title.	Size or Series.	Pages.	Date.	Price.
375	Taylor, W. B.	Origin and Nature of Force,	R. 1870,	19	1870	free
376	Hunt, T. Sterry	Chemistry of the Earth,	R. 1869,	26	1871	free
377	Babinet, M.	Diamond and Precious Stones,	R. 1870,	33	1872	free
378	Roehrig, F. L. O.	Dakota Language,	R. 1871,	19	1872	free
379	Henry, Joseph,	Eulogy on Alex. D. Bache,	R. 1870,	28	1872	free
380	Peabody, A. P.	Scientific Education of Mechanics,	R. 1872,	13	1873	free
381	Schott, C. A.	Temperature Chart of U. S. for Year, etc.,	*	1	1873	free
382	Rau, Charles,	North American Stone Implements,	R. 1872,	16	1873	
383	Bransford, J. F.	Archæological Researches in Nicaragua,	S. C.	100	1881	2.50
384	Baird, S. F.	Circular for Shipping Fresh Fish,	M. C.	4	188	free
385	Rau, Charles,	Ancient Aboriginal Trade in North America,	R. 1872,	49	1873	
386	Brezina, A.	Crystallography,	R. 1872,	36	1874	free
387	Schott, C. A.	Temperature Charts, Summer Winter, Year,	S. C. XXI,	3	1874	free
388	Schott, C. A.	Temperature Chart—Year,	*	1	1874	free
389	Henry, Joseph,	Investigation of Illuminants,	R. 1880,	25	1881	free
390	Hilgard, J. E.	Tides and Tidal Action in Harbors,	R. 1874,	22	1875	free
391		Act to Establish Smithsonian Institution,	M.C. XVIII,	10	1875	free
392	Romer, F. F.	Prehistoric Antiquities of Hungary,	R. 1876,	9	1877	
393	Gillman, Henry,	Mound-builders. Ancient Man in Michigan,	R. 1875,	13	1877	free
394	Abbott, C. C.	Stone-age in New Jersey,	R. 1875,	136	1877	free
395	Taylor, Wm. B.	Kinetic Theories of Gravitation,	R. 1876,	80	1877	free
396	McParlin, T. A.	History and Climate of New Mexico,	R. 1877,	30	1877	free
397	Mason, Otis T.	Latimer Collection of Antiquities,	R. 1876,	23	1877	free
398	Abbe C.	Meteorological Memoirs (Translations),	R. 1877,	104	1878	free

No.	Author.	Title.	Size or Series.	Pages.	Date.	Price.
399	Holmgren, F.	Color-blindness,	R. 1877,	72	1878	free
400	Jones, Chas. C.	Aboriginal Structures in Ga.,	R. 1877,	13	1878	free
401	Weismann, A.	Change of Mexican Axolotl to Amblystoma,	R. 1877,	29	1878	free
402	Rau, Charles,	Stock in-trade of Aboriginal Lapidary,	R. 1877,	9	1878	free
403	Rau, Charles,	Gold Ornament from Florida,	R. 1877,	6	1878	free
404	Haldeman, S. S.	Polychrome Bead from Florida,	R. 1877,	6	1878	free
405	Taylor, Wm. B.	Henry and the Telegraph,	R. 1878,	103	1879	free
406	Henry, Joseph,	Researches in Sound,	R. 1878,	106	1879	free
407	Gray, Asa,	Memoir of Joseph Henry,	R. 1878,	35	1879	free
408	Baird, S. F.	Report of Secretary of Smithsonian Institution for 1878,	R. 1878,	60	1879	free
409	Sherman, W. T. Parker, P. and Baird, S. F.	Report of Museum Building Commission and of the Architects for 1879,	R. 1879,	18	1880	free
410	Holden, E. S.	Reports of Astronomical Observatories for 1879,	R. 1879,	60	1880	free
411	Lautenbach, B. F.	Irritation of Polarized Nerve,	R. 1878,	59	1880	free
412	Cope, Edw. D	Zoological Position of Texas. Bull. Nat. Mus., No. 17.	M. C.	51	1880	
413	Goode, G. B.	Berlin Fishery Exhibit. Bull. Nat. Mus., No. 18.	M. C.	278	1880	
414	Schott, C. A.	Base-Chart of the U. S.	*	1	1880	.15
415	Knight, Edw. H.	Savage Weapons,	R. 1879,	90	1880	free
416		Smithsonian Miscellaneous Collections,	M. C. XIX,	1034	1880	
417	Mayer, Alfred M.	Henry as a Discoverer,	M. C. XXI,	36	1880	free
418	Baird, S. F.	Report of Secretary of Smithsonian Institution for 1879,	R. 1879,	76	1880	free
419	Baird, S. F.	Report of Secretary of Smithsonian Institution for 1880,	R. 1880,	88	1881	free
420	Mason, Otis T.	Anthropological Investigations in 1879,	R. 1879,	30	1881	free
421	Boehmer, G. H.	Index to Smithsonian Anthropological Articles,	R. 1879,	10	1881	free
422	Ridgway, Robt.	Nomenclature of N. American Birds. Bull. Nat. Mus., No. 21,	M. C.	94	1881	.25

No	Author.	Title.	Size or Series.	Pages.	Date.	Price.
423		Smithsonian Miscellaneous Collections,	M. C. xx,	846	1881	
424		Smithsonian Miscellaneous Collections,	M. C. xx,	773	1881	
425		Proceedings of National Museum for 1880. Vol. III,	M. C.	594	1881	
426	Holden, E. S. and Hastings, C. S.	Synopsis of Herschel's Writings.	R. 1880,	118	1881	free
427	Holden, E. S.	Recent Progress in Astronomy,	R. 1880,	39	1881	free
428	Hawes, G. W.	Recent Progress in Geology and Mineralogy,	R. 1880,	30	1881	free
429	Barker, G. F.	Recent Progress in Physics and Chemistry,	R. 1880,	65	1881	free
430	Farlow, W. G.	Recent Progress in Botany,	R. 1880,	19	1881	free
431	Gill, Theodore,	Recent Progress in Zoology,	R. 1880,	62	1881	free
432	Mason, Otis T.	Recent Progress in Anthropology,	R. 1880,	51	1881	free
433	Mason, Otis T.	Visit to Luray Cavern, Va.	R. 1880,	12	1881	free
434	Sherman, W. T. Parker, P. and Baird, S. F.	Report of National Museum Building Commission and of the Architects for 1880,	R. 1880,	12	1881	free
435	Loud, F. H.	Discussion of Snell's Barometric Observations,	R. 1880,	23	1881	free
436		List of Periodicals received by Smithsonian Institution,	R. 1880,	9	1881	free
437		Check List of Publications of Smithsonian Institution,	M. C.	22	1881	free
438	Holden E. S. and Boehmer, G. H.	Reports of Astronomical Observatories for 1880,	R. 1880,	128	1881	free

WORKS IN PREPARATION.

Monograph of Chitonidæ. By P. P. CARPENTER.

Bibliography of the Fishes of Western North America. By THEODORE GILL. *Bulletin of the National Museum, No. 11.*

Synopsis of the Fishes of the United States. By DAVID S. JORDAN. *Bulletin of the National Museum, No. 16.*

An Index of Names used for Zoological Genera, comprising 70,000 titles. By SAMUEL H. SCUDDER. 8vo. *Bulletin of the National Museum, No. 19.*

The Writings of American Zoologists. Index Bibliography, No. I. Publications of Spencer Fullerton Baird. By G. BROWN GOODE. 8vo. *Bulletin of the National Museum, No. 20.*

Flora of the District of Columbia. By LESTER F. WARD. *Bulletin of the National Museum, No. 22.*

Collector's Manual of Marine Zoology. By RICHARD RATHBUN. *Bulletin of the National Museum, No. 23.*

Tables showing the amount of Precipitation of Rain and Snow for each Month and Year at upwards of 2000 stations in the United States. By CHARLES A. SCHOTT and E. H. COURTENAY.

Regulations for the Telegraphic Announcement of Astronomical Discoveries. By S. F. BAIRD.

The Constants of Nature. Part V. A Revision of the Atomic Weights. By FRANK W. CLARKE.

List and Index of Publications of the Smithsonian Institution from 1846 to 1881. By WM. J. RHEES.

List of Foreign Correspondents. By GEO. H. BOEHMER.

SMITHSONIAN MISCELLANEOUS COLLECTIONS.

478

CATALOGUE OF PUBLICATIONS

OF THE

SMITHSONIAN INSTITUTION,

(1846 – 1882,)

WITH AN

ALPHABETICAL INDEX OF ARTICLES

IN THE

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE, MISCELLANEOUS COLLECTIONS, ANNUAL REPORTS, BULLETINS AND PROCEEDINGS OF THE U. S. NATIONAL MUSEUM, AND REPORT OF THE BUREAU OF ETHNOLOGY.

BY WILLIAM J. RHEES,

CHIEF CLERK OF THE INSTITUTION.

WASHINGTON:
SMITHSONIAN INSTITUTION.
1882.

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PREFACE.

The present catalogue embraces all the articles published by the Smithsonian Institution from its organization in 1846 to the first of July, 1882, a period of thirty-six years.

At the beginning nothing was issued but pamphlets explanatory of the plan of the Institution and brief annual reports of the proceedings of the Board of Regents, indicated in the catalogue by the letters A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, Q. An elaborate work, (P in the catalogue), by Robert Dale Owen, on public architecture, with special reference to the plans of the Smithsonian Institution, prepared on behalf of the Building Committee, was printed at the expense of the Institution in 1849, but did not form part of the regular series organized by the Secretary of the Institution, Prof. Henry.

1. Smithsonian Contributions to Knowledge.

The series entitled "Smithsonian Contributions to Knowledge," in quarto form, was commenced in 1848 by the publication of Squier and Davis' Ancient Monuments of the Mississippi Valley. The following "Advertisement" of the first volume, prepared by Prof. Henry, has been inserted in every succeeding volume to indicate the character and design of the series:

"This volume is intended to form the first of a series of volumes, consisting of original memoirs on different branches of knowledge published at the expense and under the direction of the Smithsonian Institution. The publication of this series forms part of a general plan adopted for carrying into effect the benevolent intentions of James Smithson, Esq., of England. This gentleman left his property in trust to the United States of America to found at Washington an institution which should bear his own name, and have for its objects 'the *increase* and *diffusion* of knowledge among men.' This trust was accepted by the Government of the United States, and an act of Congress was passed August 10, 1846, constituting the President and the other principal executive officers of the General Government, the Chief Justice of the Supreme Court, the Mayor of Washington, and such other persons as they might elect honorary members, an establishment under the name of the 'Smithsonian Institution, for the increase and diffusion of knowledge among

men.' The members and honorary members of this establishment are to hold stated and special meetings for the supervision of the affairs of the Institution and for the advice and instruction of a Board of Regents, to whom the financial and other affairs are entrusted.

"The Board of Regents consists of three members *ex-officio* of the establishment, namely, the Vice-President of the United States, the Chief Justice of the Supreme Court, and the Mayor of Washington, together with twelve other members, three of whom are appointed by the Senate from its own body, three by the House of Representatives from its members, and six citizens appointed by a joint resolution of both houses. To this Board is given the power of electing a Secretary and other officers, for conducting the active operations of the Institution.

"To carry into effect the purposes of the testator, the plan of organization should evidently embrace two objects, one, the increase of knowledge by the addition of new truths to the existing stock; the other, the diffusion of knowledge thus increased among men. No restriction is made in favor of any kind of knowledge, and hence each branch is entitled to and should receive a share of attention.

"The act of Congress, establishing the Institution, directs, as part of the plan of organization, the formation of a Library, a Museum, and a Gallery of Art, together with provisions for physical research and popular lectures, while it leaves to the Regents the power of adopting such other parts of an organization as they may deem best suited to promote the objects of the bequest.

"After much deliberation, the Regents resolved to divide the annual income, thirty thousand nine hundred and fifty dollars, into two equal parts, one part to be devoted to the increase and diffusion of knowledge by means of original research and publications, the other half of the income to be applied in accordance with the requirements of the act of Congress to the gradual formation of a Library, a Museum, and a Gallery of Art."

(The Programme of Organization, adopted December 8, 1847, follows.)

"In accordance with the rules adopted in the Programme of Organization, each memoir in this volume has been favorably reported on by a Commission appointed for its examination. It is however, impossible, in most cases, to verify the statements of an author; and, therefore, neither the Commission nor the Institution can be responsible for more than the general character of a memoir."

The total number of papers published in the 23 volumes of "Contributions" is 119, with an aggregate of 12,456 pages, 1,567 wood cuts, 523 plates, and 16 maps, each volume averaging 541½ pages.

2. Miscellaneous Collections.

In the year 1862, another series was instituted, entitled "Smithsonian Miscellaneous Collections" each volume of which has the following preface:

"The present series, entitled "Smithsonian Miscellaneous Collections," is intended to embrace all the publications issued directly by the Smithsonian

Institution in octavo form; those in quarto constituting the "Smithsonian Contributions to Knowledge." The quarto series includes memoirs, embracing the records of extended original investigations and researches, resulting in what are believed to be new truths, and constituting positive additions to the sum of human knowledge. The octavo series is designed to contain reports on the present state of our knowledge of particular branches of science; instructions for collecting and digesting facts and materials for research: lists and synopses of species of the organic and inorganic world; museum catalogues; reports of explorations; aids to bibliographical investigations, etc.; generally prepared at the express request of the Institution and at its expense.

"The position of a work in one or the other of the two series will sometimes depend upon whether the required illustrations can be presented more conveniently in the quarto or the octavo form.

"In the Smithsonian Contributions to Knowledge, as well as in the present series, each article is separately paged and indexed, and the actual date of its publication is that given on its special title page, and not that of the volume in which it is placed. In many cases works have been published and largely distributed years before their combination into volumes.

"While due care is taken on the part of the Smithsonian Institution to insure a proper standard of excellence in its publications, it will be readily understood that it cannot hold itself responsible for the facts and conclusions of the authors, as it is impossible in most cases to verify their statements."

The total number of papers published in the 23 volumes of "Miscellaneous Collections" is 122, each volume averaging 882½ pages, with an aggregate of 20,299 pages, 2,868 wood cuts, and 43 plates.

3. Annual Reports.

By the act of Congress organizing the Institution it was made the duty of the "Board of Regents to submit at each session a report of the operations, expenditures, and condition of the Institution." These Annual Reports form a third series of Smithsonian publications. They consist of the reports of the Secretary to the Board of Regents of the operations and condition of the Institution; the reports of committees of the Board; reports of lectures; extracts from correspondence; original or translated articles relating to the history and progress of science, etc.

The first report was submitted by the Board to the second session of the 29th Congress, 1847, and formed an octavo pamphlet of 38 pages. A similar report was presented annually thereafter, varying in size from 64 pages to 326, printed in pamphlet form with paper covers up to 1853, when Congress ordered the report to be bound in cloth. In the volume for that year the essential portion of the contents of the preceding seven reports was reprinted,

and this is now considered as the first of a set of Smithsonian Reports. The number of pages was limited between 1854 and 1876 to 400. In the latter year this restriction was removed, and since then the average number of pages has been 600.

The number of copies of these reports for general distribution ordered by Congress has been very variable, the largest being 7,500 in 1874 and 1875, and the smallest 150 in 1847. The number of copies granted the Institution each year is shown in the following table:

Number of extra copies furnished the Institution by Congress for distribution.

For the Year.	No. of Copies.	For the Year.	No. of Copies.	For the Year.	No. of Copies.
1847	150	1859	2,000	1871	5,000
1848	1,000	1860	2,000	1872	5,000
1849	500	1861	2,000	1873	6,000
1850	1,000	1862	2,000	1874	7,500
1851	2,000	1863	2,000	1875	7,500
1852	2,000	1864	2,000	1876	6,500
1853	3,000	1865	2,000	1877	6,500
1854	2,500	1866	2,000	1878	6,500
1855	2,500	1867	2,000	1879	7,000
1856	2,500	1868	2,000	1880	7,000
1857	5,000	1869	3,000		
1858	5,000	1870	5,000		

The total number of pages in the 35 volumes of Annual Reports is 14,419, average 412 pages; total number of woodcuts, 1,898.

4. Bulletins of the U. S. National Museum.

In the year 1875 a fourth series of publications (octavo) was commenced, entitled "Bulletins of the National Museum," intended to illustrate the collections of natural history and ethnology belonging to the United States, constituting the National Museum, of which the Smithsonian Institution is the custodian.

Twenty of these Bulletins have been published, with an aggregate of 3,103 pages, 45 plates, and 1 map.

5. Proceedings of the U. S. National Museum.

In imitation of the practice of those learned societies which publish periodically descriptions of new species, &c., in the form of proceedings of weekly or monthly meetings, and thus present to the world the discoveries connected with the establishment at the earliest practicable moment, it appeared to be very desirable that the National Museum should have some medium of prompt publication for announcing descriptions of specimens received, (many of which are new species,) as well as other interesting facts relative to natural history furnished by correspondents of the Institution. To meet this want a fifth series of publications, (octavo,) entitled "Proceedings of the National Museum," was commenced in 1880. They are printed in successive signatures as fast as material sufficient for 16 pages is prepared, and distributed at once to scientific societies and leading active working naturalists in this country and in Europe,* each signature having printed at the bottom of its first page the date of actual issue, for settling any questions as to priority of publication. Of this series four volumes have been published, comprising 2,221 pages, with 28 cuts and 19 plates.

6. Reports of the Bureau of Ethnology.

The sixth series of publications is the annual report (in Imperial octavo) of the Bureau of Ethnology, placed by Congress in charge of the Smithsonian Institution. The first volume of this series was issued in 1881, and consists of 638 pages, with 343 cuts, 54 plates, and 1 map.

The distribution of this volume to individuals is wholly by Members of Congress and the Director of the Bureau, Major J. W. Powell—the Institution having copies at its disposal only for the libraries on its regular list of distribution for its own full series.

7. Copyright.

No copyright has ever been secured on the publications of the Institution. They are left free to be used by compilers of books without any restrictions, except that full credit shall be given to the name of Smithson for any extracts which may be made from them.

* Prof. Baird's report for 1880.

8. Use of Illustrations.

Copies of the wood cuts used by the Institution are granted to authors or publishers on payment of the actual cost of production of electrotypes, and promise to give proper reference to the article in which they originally appeared.

9. Size of Editions.

In the first experiments of the Smithsonian system of publication, the proper magnitude of the editions necessary to meet the immediate and future demand could not be accurately ascertained. The number of copies of the Contributions then fixed upon, has since been found inadequate, although it was larger than that usually issued by other institutions. The edition has, therefore, been augmented, until at the present time 1,000 copies of each article are set aside to be combined into volumes, and an extra number, varying with the probable demand, struck off for separate distribution, and for sale.

Each article is complete in itself, with separate paging, title, and index, and without any necessary relationship to others combined with it in the same volume.

Of the early volumes of Smithsonian Contributions, the edition, for reasons already explained, was less than of the succeeding ones, so that complete sets cannot now be furnished.

In the year 1862, the plan of stereotyping every article printed by the Institution was adopted, the plates being carefully preserved, thus making it practicable at any time to issue new editions except where expensive lithographic plates were used, a limited number, only, of impressions from these having been taken.

A number of the earlier articles in octavo were out of print before the commencement of the series of "Miscellaneous Collections," and consequently are not included in them.

The printing of the "Bulletins" and "Proceedings" is authorized by the Department of the Interior and paid for out of its fund. An edition of 1,000 copies is published, of which one-half is distributed by the Department of the Interior and one-half by the Institution. As the pages are stereotyped, the cost of additional copies is slight; and for the purpose of making sure that a sufficient number of sets will be accessible forever to

students in all parts of the world, it has been considered expedient to print 1,500 additional copies of each for incorporation in the Miscellaneous Collections.*

10. Distribution of Publications.

The distribution of the publications of the Institution is a matter which requires much care and judicious selection, the great object being to make known to the world the truths which may result from the expenditure of the Smithson fund. For this purpose the Contributions are so distributed as to be accessible to the greatest number of readers; that is, to large central libraries.

The volumes of Contributions are presented on the express condition that, while they are carefully preserved, they shall be accessible at all times to students and others who may desire to consult them, and be returned to the Institution in case the establishments to which they are presented at any time cease to exist.

These works, it must be recollected, are not of a popular character, but require profound study to fully understand them; they are, however, of importance to the professional teacher and the popular expounder of science. They contain the materials from which general treatises on special subjects may be elaborated.†

Full sets of the publications cannot be given to all who apply for them, since this is impossible with the limited income of the Institution, and, indeed, if care be not exercised in the distribution, so large a portion of the income will be annually expended on the production of copies for distribution of what has already been published that nothing further can be done in the way of new publications. It must be recollected that every addition to the list of distribution not only involves the giving of the publications which have already been made, but also of those which are to be made hereafter.‡

The rules governing the distribution of the Smithsonian publications are appended. To enable institutions not coming within their provisos, as well as individuals, to procure copies of such as may be desired, a small number is set aside and sold by the Institution at a price which is intended merely to cover the actual cost of their publication.

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* Prof. Baird's report for 1880.

† Prof. Henry's report for 1876.

‡ Prof. Henry's report for 1873.

11. Rules for Distribution of the Publications of the Smithsonian Institution.

To Institutions.

The publications of the Smithsonian Institution are furnished:

1st. To learned societies of the first class, which present complete series of their publications to the Institution.

2d. To libraries of the first class, which give in exchange their catalogues and other publications; or an equivalent, from their duplicate volumes.

3d. To colleges of the first class, which furnish catalogues of their libraries and of their students, and all publications relative to their organization and history.

4th. To public libraries containing 25,000 volumes.

5th. To smaller public libraries, where a large district would be otherwise unsupplied.

6th. Institutions devoted exclusively to the promotion of particular branches of knowledge may receive such Smithsonian publications as relate to their respective objects.

To Individuals.

The gratuitous distribution to *individuals*, of the publications of the Institution, is restricted:

1st. To those who are engaged in original research in the branch of science to which the book asked for pertains.

2d. To those who require it in the business of instruction.

3d. To donors to the museum or library of the Institution.

12. Form of Application for Publications.

To the Smithsonian Institution, Washington, D. C.

Date, 18

In behalf of the , we respectfully apply for the publications of the Smithsonian Institution, on condition that all volumes received shall be carefully preserved, be accessible to any person who may wish to consult them, and be returned to the Smithsonian Institution in case the establishment at any time ceases to exist.

1. Name of Establishment --
2. Location—Town --

   State --
3. When established --
4. Character --
5. Buildings and property --
6. Permanent fund --
7. Annual income --
8. Volumes in library --
9. Number of persons having use of books --
10. Date of last catalogue of library --
11. What publications made --

    (Send printed list if possible.)
12. Names of Officers: President --

    Secretary --

    Librarian --
13. Addresses of principal scientific men connected with the Establishment and subjects in which specially interested --

I recommend the above application.

-- *Member of Congress,*

-- *District* -- *State.*

13. Price List of Smithsonian Publications.

Where no price is given the work is out of print, and cannot be furnished. Of those marked "free" the edition is limited, and copies are only given to those specially interested in the subjects to which they pertain, who are collaborators of the Institution or contributors to its library or museum.

P	$10 00	60	$1 00	120	$1 00	180	$1 00	240		300	$0 25	360	free.	420	free.
1		61	1 00	121	25	181	2 00	241	$7 50	301		361		421	free.
2		62	2 00	122	6 00	182	2 50	242	7 50	302	25	362	free.	422	$0 25
3		63	1 00	123	6 00	183	25	243	free.	303	50	363	free.	423	6 00
4		64	free.	124		184	12 00	244	1 00	304	50	364	free.	424	6 00
5		65		125	6 00	185	free.	245	free.	305	50	365	free.	425	2 00
6		66		126	1 25	186	50	246	12 00	306	50	366	free.	426	free.
7		67		127	1 25	187	50	247	50	307		367	free.	427	free.
8		68		128	25	188	50	248		308	50	368		428	free.
9		69		129	1 00	189	1 00	249		309	free.	369		429	free.
10		70	6 00	130	1 50	190	free.	250		310	25	370	free.	430	free.
11		71		131	1 25	191		251	free.	311	50	371	free.	431	free.
12	4 00	72	3 00	132	25	192	5 00	252		312		372	free.	432	free.
13	2 00	73	25	133	2 00	193	free.	253		313	50	373	free.	433	free.
14	1 00	74		134		194		254	2 00	314	6 00	374	free.	434	free.
15	4 00	75		135		195		255		315	6 00	375	free.	435	free.
16		76	12 00	136		196		256	2 00	316	free.	376	free.	436	free.
17	50	77		137		197	1 00	257		317	3 00	377	free.	437	free.
18		78	12 00	138	free.	198		258	2 00	318	2 00	378	free.	438	free.
19		79	1 00	139	free.	199	2 00	259	3 00	319	free.	379	free.	439	35
20	1 00	80	1 00	140	75	200	25	260		320	free.	380	free.	440	50
21	1 00	81		141	1 50	201	50	261	free.	321	25	381	free.	441	1 50
22		82	1 50	142	3 00	202	3 50	262	3 00	322	6 00	382	free.	442	50
23	2 00	83	1 25	143	1 25	203		263		323		383	$2 50	443	1 00
24		84	1 50	144	1 00	204	1 00	264		324	free.	384	free.	444	50
25	50	85	25	145	75	205	free.	265		325	free.	385	free.	445	free.
26		86		146	1 50	206	12 00	266	25	326	50	386	free.	446	free.
27	50	87	25	147		207	free.	267	1 00	327	75	387	free.	447	free.
28	1 00	88	1 00	148	free.	208	50	268		328	5 00	388	free.	448	free.
29		89	5 00	149		209		269		329		389	free.	449	free.
30		90	5 00	150		210	25	270	2 00	330		390	free.	450	free.
31		91		151	12 00	211	12 00	271		331	2 00	391	free.	451	free.
32		92	12 00	152		212	6 00	272	12 00	332	2 00	392	free.	452	free.
33	75	93		153		213	6 00	273	6 00	333	2 00	393	free.	453	free.
34	free.	94	50	154		214	1 00	274	6 00	334	25	394	free.	454	free.
35		95	6 00	155		215		275	50	335	free.	395	free.	455	free.
36	1 00	96	20 00	156	50	216	25	276	50	336	6 00	396	free.	456	free.
37		97	1 00	157		217		277	3 00	337	6 00	397	free.	457	free.
38		98	4 00	158		218		278	free.	338		398	free.	458	free.
39		99	12 00	159	1 00	219	2 00	279	25	339		399	free.	459	free.
40		100	50	160		220		280	1 00	340	12 00	400	free.	460	free.
41	1 00	101	free.	161	50	221	1 00	281	75	341	50	401	free.	461	free.
42		102		162	1 00	222	3 00	282	25	342	50	402	free.	462	free.
43		103	2 00	163	free.	223	1 00	283	25	343	free.	403	free.	463	50
44		104		164	50	224		284	12 00	344	free.	404	free.	464	free.
45		105	50	165		225		285	12 00	345	50	405	free.	465	free.
46		106	50	166	1 00	226	free.	286	50	346	12 00	406	free.	466	free.
47	50	107		167	1 00	227	25	287	2 00	347	free.	407		467	2 00
48		108	25	168	free.	228	50	288	50	348		408	free.	468	6 00
49	1 00	109		169	6 00	229	12 00	289	50	349	25	409	free.	469	free.
50	1 50	110		170	free.	230	25	290	free.	350	free.	410	free.	470	50
51		111	12 00	171		231		291	25	351		411	free.	471	free.
52	5 00	112	12 00	172		232	2 00	292	50	352	free.	412	50	472	free.
53	50	113	25	173	2 50	233	25	293	50	353	3 00	413	50	473	free.
54	50	114	1 25	174	2 00	234	free.	294	50	354	free.	414	15	474	free.
55		115	free.	175	1 00	235	free.	295	50	355		415	free.	475	6 00
56		116		176	free.	236	free.	296	50	356	50	416	6 00	476	
57	1 00	117	2 00	177	25	237	free.	297	50	357	2 50	417	free.	477	free.
58	5 00	118	1 00	178	free.	238	free.	298	50	358	1 00	418	free.	478	75
59	25	119	1 00	179	3 00	239	2 00	299		359	free.	419	free.		

LIST OF PUBLICATIONS

OF THE

SMITHSONIAN INSTITUTION.

NOTE.—A to Q indicate early publications not embraced in the regular series.

A. Journal of Proceedings of the Regents of the Smithsonian Institution, at the city of Washington, beginning on the first Monday of September, 1846. 1846. 8vo., pp. 32.

B. Report of the Organization Committee of the Smithsonian Institution, with the resolutions accompanying the same and adopted by the Board of Regents; also, the Will of the testator, the Act accepting the bequest, and the Act organizing the Institution. 1847. 8vo., pp. 32.

C. Digest of the Act of Congress establishing the Smithsonian Institution. August 10, 1846. 8vo., pp. 8.

D. Address delivered on occasion of laying the Corner Stone of the Smithsonian Institution, May 1, 1847. By GEORGE M. DALLAS, Chancellor of the Institution. 1847. 8vo., pp. 8.

E. Smithson's Bequest. Professor HENRY'S exposition before the New Jersey Historical Society, at its meeting in Princeton, on Wednesday, September 27. 1847. 8vo., pp. 8.

F. First Report of the Secretary of the Smithsonian Institution to the Board of Regents; giving a Programme of Organization, and an account of the operations during the year. Presented December 8, 1847. 1848. 8vo., pp. 48.

G. [First] Report from the Board of Regents, submitted to Congress, of the operations, expenditures, and condition of the Smithsonian Institution. Senate Doc. 211; 29th Congress, 2d Session. 1847. 8vo., pp. 38.

H. Second Report of the Board of Regents of the Smithsonian Institution, to the Senate and House of Representatives, showing the operations, expenditures, and condition of the Institution during the year 1847. 30th Congress, 1st Session. Senate Miscellaneous No. 23. 1848. 8vo., pp. 208.

H. Report for 1847—Continued.

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Report of Prof. J. Henry, and Proceedings of the Board.

Gallatin, A.; Robinson, E.; Bartlett, J. R.; Turner, W. W.; Morton, S. G.; Marsh, G. P. On publication of Squier & Davis's Ancient Monuments.

Jewett, C. C. Report on plan of library.

Loomis, E. Report on meteorology of the United States.

Espy, J. P. On meteorology.

I. Third Annual Report of the Board of Regents of the Smithsonian Institution, for the year 1848. 30th Congress, 2d Session. H. R. Miscellaneous, No. 48. 1849. 8vo., pp. 64.

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Report of Prof. J. Henry, and Proceedings of the Board.

Jewett, C. C. Report on library.

Stevens, H. Prospectus of a Bibliographia Americana.

Hare, R. Letter relative to gift of apparatus.

Guyot, A. On metric system for scientific observations.

J. Programme of organization of the Smithsonian Institution. Presented in the first annual report of the Secretary, and adopted by the Board of Regents, December 13, 1847. 1847. 4to., pp. 4.

K. Correspondence relative to the acceptance for publication of the ethnological memoir of Messrs. Squier and Davis. 1847. 8vo., pp. 8.

L. [First] Report of the Organization Committee of the Smithsonian Institution. Reprinted from the National Intelligencer, December 8, 1846. 8vo., pp. 8.

M. Reports, etc., of the Smithsonian Institution, exhibiting its plans, operations, and financial condition up to January 1, 1849. From the third annual report of the Board of Regents. Presented to Congress February 19, 1849. 1849. 8vo., pp. 72.

N. Officers and Regents of the Smithsonian Institution, with the act of Congress accepting the bequest, and the act incorporating said Institution. 1846. 8vo., pp. 14.

O. An Act to establish the Smithsonian Institution. Approved Aug. 10, 1846. pp. 8.

P. Hints on Public Architecture, containing, among other illustrations, views and plans of the Smithsonian Institution; together with an appendix relative to building materials. Prepared on behalf of the Building Committee of the Smithsonian Institution, by Robert Dale Owen, chairman of the committee. 1849. 4to., pp. 140, 99 woodcuts, 15 plates.

Q. Check list of periodical publications received in the reading-room of the Smithsonian Institution, for the year 1853. 1853. 4to., pp. 28.

REGULAR SERIES.

1. Ancient Monuments of the Mississippi Valley; comprising the results of extensive original surveys and explorations. By E. G. SQUIER and E. H. DAVIS. 1848. 4to., pp. 346, 207 woodcuts, 48 plates. (S. C. I.)

2. Smithsonian Contributions to Knowledge. Vol. I. 1848. 4to., pp. 360, 207 woodcuts, 48 plates.

CONTENTS.

SQUIER and DAVIS. Ancient Monuments, Mississippi Valley. No. 1.

3. Researches relative to the Planet Neptune. By SEARS C. WALKER. 1849. 4to., pp. 60. (S. C. II.)

4. Ephemeris of the Planet Neptune for the Opposition of 1848. By SEARS C. WALKER. 1848. 4to, pp. 8. (S. C. II.)

5. Ephemeris of the Planet Neptune from the date of the Lalande Observations of May 8 and 10, 1795, and for the Opposition of 1846, '47, '48, and '49. By SEARS C. WALKER. April, 1849. 4to., pp. 32. (S. C. II.)

6. Ephemeris of the Planet Neptune for the year 1850. By SEARS C. WALKER. April, 1850. 4to., pp. 10. (S. C. II)

7. Ephemeris of the Planet Neptune for the year 1851. By SEARS C. WALKER. December, 1850. 4to., pp. 10. (S. C. II.)

8. *Occultations visible in the United States during the year 1848. By JOHN DOWNES. 1848. 4to., pp. 12.

9. *Occultations visible in the United States during the year 1849. By JOHN DOWNES. 1848. 4to., pp. 24.

10. *Occultations visible in the United States during the year 1850. By JOHN DOWNES. 1849. 4to., pp. 26.

11. Occultations visible in the United States during the year 1851. By JOHN DOWNES. October, 1850. 4to., pp. 26. (S. C. II.)

12. On the Vocal Sounds of Laura Bridgman, the Blind Deaf Mute at Boston; compared with the Elements of Phonetic Language. By FRANCIS LIEBER. 1850. 4to., pp. 32, one plate. (S. C. II.)

13. Contributions to the Physical Geography of the United States. Part I. On the physical geography of the Mississippi valley, with suggestions for the improvement of the navigation of the Ohio and,

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* These three papers by Mr. Downes, Nos. 8, 9, 10, were not published in the series of Contributions.

other rivers. By CHARLES ELLET, JR. 1850. 4to., pp. 64, 2 woodcuts, 1 plate. (S. C. II.)

14. A Memoir on *Mosasaurus*, and the three Allied New Genera, *Holcodus*, *Conosaurus*, and *Amphorosteus*. By ROBERT W. GIBBES. November, 1850. 4to., pp. 14, 3 plates of 28 figures. (S. C. II.)

15. Aboriginal Monuments of the State of New York. Comprising the results of original surveys and explorations; with an illustrative appendix. By E. G. SQUIER. 1850. 4to., pp. 188, 79 woodcuts, 14 plates of 33 figures. (S. C. II.)

16. The Classification of Insects from Embryological Data. By LOUIS AGASSIZ, 1850. 4to., pp. 28, 8 woodcuts, one plate of 23 figures. (S. C. II.)

17. Memoir on the Explosiveness of Nitre, with a view to elucidate its agency in the tremendous explosion of July, 1845, in New York. By ROBERT HARE. 1850. 4to., pp. 20. (S. C. II.)

18. Report on the History of the Discovery of Neptune. By BENJAMIN APTHORP GOULD, JR. 1850. 8vo., pp. 56.

19. Directions for Meteorological Observations, intended for the first class of observers. By ARNOLD GUYOT. 1850. 8vo., pp. 40, 9 woodcuts.

20. Microscopical Examination of Soundings, made by the United States Coast Survey off the Atlantic coast of the United States. By J. W. BAILEY. January, 1851. 4to., pp. 16 and 1 plate of 68 figures. (S. C. II.)

21. Fourth Annual Report of the Board of Regents of the Smithsonian Institution, for the year 1849. 31st Congress, 1st Session. Senate Miscellaneous No. 120, 8vo., pp. 64, with appendix of 207 pp. House of Representatives Miscellaneous No. 50. 1850. 8vo., pp. 272.

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Report of Prof. J. HENRY, and Proceedings of the Board.

GRAY, ASA. Account of Lindheimer's, Fendler's and Wright's botanical explorations in New Mexico and California.

AGASSIZ, LOUIS. On the formation of a museum.

List of meteorological observers.

JEWETT, C. C. Report on library and catalogue system.

JEWETT, C. C. Report on public libraries of the United States.

22. Plantæ Wrightianæ Texano-Neo-Mexicanæ. By ASA GRAY. Part I. March, 1852. 4to., pp. 146, 10 plates of 127 figures. (S. C. III.)

An account of a collection of plants made by Charles Wright in Western Texas, New Mexico, and Sonora, in the years 1851 and 1852.

23. Microscopical Observations made in South Carolina, Georgia, and Florida. By J. W. BAILEY. 1851. 4to., pp. 48, 3 plates of 83 figures. (S. C. II.)

24. Ephemeris of the Planet Neptune for the year 1852. By SEARS C WALKER. 1853. 4to. pp. 10. (S. C. III.)

25. Notices of Public Libraries in the United States of America. By CHAS. C. JEWETT. Printed by order of Congress as an appendix to the Fourth Annual Report of the Board of Regents of the Smithsonian Institution. 1851. 8vo., pp. 210.

26. Smithsonian Contributions to Knowledge. Vol. II. 1851. 4to., pp. 572, 89 woodcuts, 24 plates.

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WALKER, S. C. Researches relative to Neptune. No. 3.
LIEBER, F. Vocal sounds of Laura Bridgman. No. 12.
BAILEY. J. W. Microscopical soundings off Atlantic Coast. No. 20.
ELLET, C. Physical geography of the Mississippi Valley. No. 13.
GIBBES, R. W. Mosasaurus and three allied genera. No. 14.
AGASSIZ, L. Classification of insects from embryological data. No. 16.
HARE, R. Explosiveness of nitre. No. 17.
BAILEY, J. W. Microscopical observations in S. C., Ga., Fla. No. 23.
SQUIER, E. G. Aboriginal monuments of State of New York. No. 15.
WALKER, S. C. Ephemeris of Neptune for 1848. No. 4.
WALKER, S. C. Ephemeris of Neptune for 1846, '47, '48, '49. No. 5.
WALKER, S. C. Ephemeris of Neptune for 1850. No. 6.
WALKER, S. C. Ephemeris of Neptune for 1851. No. 7.
DOWNES, J. Occultations visible in the United States in 1851. No. 11.

27. On Recent Improvements in the Chemical Arts. By JAMES C. BOOTH and CAMPBELL MORFIT. 1852. 8vo., pp. 216. (M. C. II.)

28. Fifth Annual Report of the Board of Regents of the Smithsonian Institution, for the year 1850. Special session, March, 1851. Senate Miscellaneous No. 1. 1851. 8vo., pp. 145. (Extra edition of 326 pp.)

CONTENTS.

Report of Prof. J. HENRY, and Proceedings of the Board.
JEWETT, C. C. General catalogue system for libraries.
BAIRD, S. F. Report on museum, and statistics of British Museum.
Memorial of the Regents to Congress, relative to the Smithson Fund.
SQUIER, E. G. Antiquities of Nicaragua.
Report of Commission on General Stereotype Catalogue of Pub. Libraries.
CULBERTSON, T. A. Expedition to the Mauvaises Terres and Upper Missouri.
PORTER, T. C. List of plants of Upper Missouri.
HARRIS, E. List of birds and mammalia of Missouri river.
CULBERTSON, T. A. Indian tribes of the Upper Missouri.
JEWETT, C. C. Copyright books from 1846–1849.

29. Occultations visible in the United States during the year 1852. By JOHN DOWNES. 1851. 4to., pp. 34. (S. C. III.)

30. Contributions to the Natural History of the Fresh Water Fishes of North America. By CHARLES GIRARD. Part I.—A monograph of the Cottoids. December, 1851. 4to., pp. 80, 3 plates of 48 figures. (S. C. III.)

31. A Collection of Meteorological Tables, with other tables useful in Practical Meteorology. By ARNOLD GUYOT. 1852. 8vo., pp. 212.

32. Nereis Boreali-Americana: or, Contributions to a History of the Marine Algæ of North America. By WILLIAM HENRY HARVEY. Part I.—Melanospermeæ. January, 1852. 4to., pp. 152, 12 colored plates of 29 figures. (S. C. III.)

33. The Law of Deposit of the Flood Tide: its Dynamical Action and Office. By CHARLES HENRY DAVIS. 1852. 4to., pp. 14. (S. C. III.)

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OF THE

SMITHSONIAN INSTITUTION.

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